PB84-128313

Air Pollution Effects on Terrestrial Ecosystems

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Jun 83

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-128313

EPA-600/6-83-003
June 1983

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by

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Office of Health and Environmental Assessment
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Research Triangle Park, N.C. 27711

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/6-83-003

2.

3. RECIPIENT'S ACCESSION NO. PB84 128313

4. TITLE AND SUBTITLE
Air Pollution Effects on Terrestrial Ecosystems

5. REPORT DATE June 1983

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J.H.B. Garner, R.W. Elias, J. M. Davis, and
F.V. Bradow

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental Criteria and Assessment Office (MD-52)
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Office of Research and Development
Office of Health and Environmental Assessment
401 M Street, S.W., Washington, D.C. 20460

13. TYPE OF REPORT AND PERIOD COVERED Final

14. SPONSORING AGENCY CODE EPA/600/00

15. SUPPLEMENTARY NOTES
This report was prepared for Panel 3, Environemntal Impact of the NATO/CCMS pilot study on air pollution control strategies and impact modeling.

16. ABSTRACT

This report presents information on the effects of ozone, nitrogen oxides, sulfur oxides, particulate matter, and acidic disposition on terrestrial ecosystems. A brief explanation of ecosystem dynamics is presented to provide a framework for discussion of air pollutant effects. Deposition processes, routes, and mechanisms of entry into plants, and responses of natural ecosystems versus agroecosystems are presented. Effects of air pollutants, singly or in combination are described in terms of dose-response relationships to the extent that supporting evidence is available. Both adverse and beneficial effects, where appropriate, are addressed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
Release to public

19. SECURITY CLASS *(This Report)* Unclassified

20. SECURITY CLASS *(This page)* Unclassified

21. NO. OF PAGES 262

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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1. INTRODUCTION

Terrestrial ecosystems comprise associations or communities of land-dwelling plant and animal species (including man) and their environments. Of particular interest from the standpoint of air pollution impacts are forest and agricultural ecosystems. These systems not only hold obvious economic significance for human society, but they also represent the even more fundamental fact that human life depends, ultimately, on such systems. Without plants at the base of the food chain, humans -- indeed all animals -- could not survive for more than a limited period of time. Thus, any detrimental effects of atmospheric pollutants on terrestrial ecosystems deserve careful attention.

There are many materials that can contaminate the environment. These materials may be emitted by natural sources, such as volcanoes and forest fires, or as a result of human activity, such as industrial processes and fuel combustion. Some of the more important pollutants are listed in Table 1-1 and are classified by their form. Generally speaking, the significance of a given pollutant is a function of (1) its relative quantity, i.e., how much its concentration exceeds normal amounts, and (2) its degree of influence on biological processes and components of the environment. This report will address some of the more significant pollutants affecting terrestrial ecosystems: particulate matter, sulfur oxides, nitrogen oxides, ozone, and acidic deposition.

Airborne particles exist in a diversity of sizes and compositions that can vary widely depending on the source and meteorological conditions. In broad terms, airborne particles tend to cluster in two principal size groups: coarse particles, generally larger than 2 to 3 micrometers (μm) in diameter;

TABLE 1-1. Materials of Importance That Pollute the Troposphere[a]

- I. Particulate pollutants
  - A. Primary
    - 1. Inorganic
      - a. Variable (dust, asbestos, soil, salt)
      - b. Chlorides
      - c. Fluorides
      - d. Trace metals
    - 2. Organic
      - a. Spores
      - b. Pollen
  - B. Secondary
    - 1. Inorganic
      - a. Sulfates
      - b. Nitrates
    - 2. Organic
      - a. Hydrocarbons
      - b. Aliphatic nitrates
      - c. Carboxylic acids
      - d. Dicarboxylic acids
- II. Gaseous pollutants
  - A. Primary
    - 1. Inorganic
      - a. Oxides
        - i. Carbon
        - ii. Sulfur
        - iii. Nitrogen
      - b. Halogens
        - i. Chloride
        - ii. Fluoride
      - c. Other
        - i. Ammonia
        - ii. Hydrogen sulfide
    - 2. Organic
      - a. Hydrocarbons
      - b. Ketones
      - c. Mercaptans
      - d. Sulfides
      - e. Halocarbons
  - B. Secondary
    - 1. Inorganic
      - a. Ozone
    - 2. Organic
      - a. Aldehydes
      - b. Peroxyacetylnitrate and homologues
      - c. N-nitroso compounds

---

[a] Materials released directly into the atmosphere are designated primary, while those synthesized in the atmosphere are termed secondary. Smith, 1981.

and fine particles, generally smaller than 2 to 3 µm in diameter. The dividing line between the coarse and the fine sizes is frequently given as 2.5 µm, but chemical composition based on the dividing line is neither sharp nor fixed and can depend on the contributing source, on meteorology, and on the age of the aerosol.

Fine particle volume (or mass) distributions may exhibit two modes: 1) the nuclei mode (which includes particles from 0.005 to 0.05 µm in diameter) formed near sources due to the condensation of vapors produced by high temperature processes such as fossil-fuel combustion; 2) the accumulation mode (which includes particles from 0.05 to about 2 µm in diameter) formed principally by coagulation or growth of the short-lived particles in the nuclei mode through vapor condensation. Typically, 80 percent or more of the atmospheric sulfate mass occurs in the accumulation mode. Accumulation-mode particles normally do not grow into coarse particles. Coarse particles include re-entrained surface dust, salt spray, and particles formed by mechanical processes, such as grinding.

Primary particles are directly discharged from manmade or natural sources. Secondary particles form by chemical and physical reactions in the atmosphere, and most of the reactants involved are emitted to the air as gaseous pollutants.

In the atmosphere, particle growth and chemical transformation occur through gas-particle and particle-particle interactions. Gas-particle interactions include condensation of low vapor pressure molecules, such as sulfuric acid (H_2SO_4) and organic compounds; such condensation occurs principally on fine particles. The only particle-particle interaction important in atmospheric processes is coagulation among fine particles.

As shown in Figure 1-1, major components of fine atmospheric particles include sulfates, carbonaceous material, ammonium, lead, and nitrate. Coarse

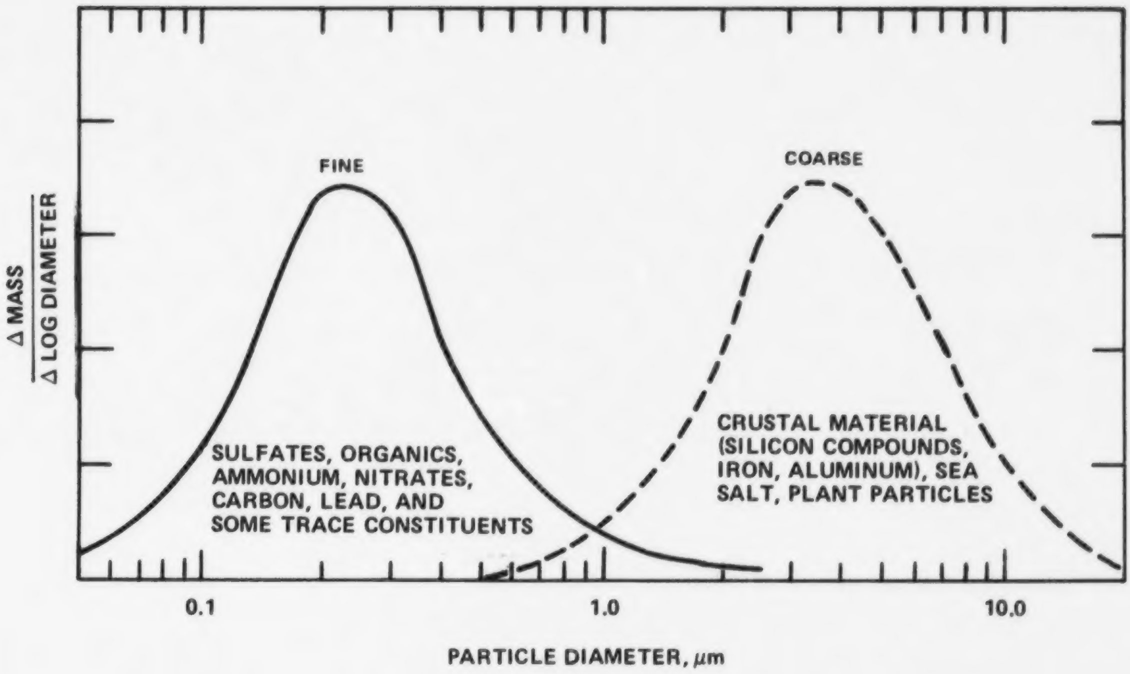

Figure 1-1. Idealized representation of typical fine- and coarse-particle mass and chemical composition distribution in an urban aerosol. Although some overlap exists, note substantial differences in chemical composition of fine versus coarse modes. Chemical species of each mode are listed in approximate order of relative mass contribution. Note that the ordinate is linear and not logarithmic.

particles consist mainly of oxides of silicon, aluminum, calcium, and iron, as well as calcium carbonate, tire particles, vegetation-related particles (e.g., pollen, spores), and sea salt. Note that the distributions of fine and coarse particles overlap and that some chemical species found predominantly in one mode may also be found in the other mode.

The carbonaceous component of fine particles contains both elemental carbon (graphite and soot) and nonvolatile organic carbon (hydrocarbons emitted in combustion exhaust and secondary organics formed by photochemistry). In many urban and nonurban areas, these species may be the most abundant fine particles after sulfates. Secondary organic particles are formed through the oxidation of primary organics via a cycle that also involves ozone and nitrogen oxides. Atmospheric reactions of nitrogen oxides may yield nitric acid vapor (HNO_3) that can accumulate as nitrate particles in both the fine and coarse modes. Details of the chemical pathways for forming nitrate particles and secondary organics are not well established, and the validity of historical nitrate data is questionable.

Most atmospheric sulfates and nitrates are water-soluble and have a tendency to absorb moisture. Hygroscopic growth of sulfate-containing particles has a profound effect on their size, reactivity, and other physical properties which in turn influence their biological and physical effects.

Of the four known sulfur oxides (sulfur monoxide, sulfur dioxide, sulfur trioxide, and disulfur monoxide), only sulfur dioxide occurs at significant concentrations in the atmosphere. A colorless gas with a pungent odor, SO_2 is emitted from combustion of sulfur-containing fossil fuels, such as coal and oil, as well as from many other sources.

Sulfur dioxide is removed from the atmosphere by gaseous transformation, aqueous, and surface oxidation to form acidic sulfates. Also important are physical removal pathways for SO_2, such as dissolution in raindrops and dry deposition on the earth's surface. Gas-phase oxidation of SO_2 by the hydroxyl (OH) radical is well understood; not so well understood, however, is the oxidation of SO_2 by hydroperoxyl (HO_2) and methylperoxyl (CH_3O_2) radicals. The ready solubility of SO_2 in water is due principally to the formation of bisulfite (HSO_3^-) and sulfite (SO_3^{-2}) ions, which in turn are easily oxidized to form acidic sulfates by reacting with catalytic metal ions and dissolved oxidants. The aqueous-phase oxidation reactions are very complex, and the metal ion catalytic reactions are poorly understood. On the other hand, the oxidation of HSO_3^- and SO_3^{2-} by dissolved hydrogen peroxide (H_2O_2) and ozone (O_3) is well understood; for most situations in the lower troposphere, it appears that oxidation by dissolved H_2O_2 is more important than oxidation by dissolved O_3. Sulfur dioxide reacts on the surface of a variety of airborne solid particles, such as ferric oxide, lead dioxide, aluminum oxide, salt, and charcoal. At this time, however, adequate information on the relative importance of the various pathways and on all of the significant reaction rates for SO_2 oxidation in the lower troposphere is not available.

There are eight nitrogen oxides which may be present in the ambient air: nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), unsymmetrical nitrogen trioxide (OONO), symmetrical nitrogen trioxide (O-N(O)-O), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4), and dinitrogen pentoxide (N_2O_5).

Of these, NO and NO_2 are generally considered the most important in the lower troposphere because in polluted atmospheres they may be present in significant concentrations. Their interconvertibility in photochemical smog reactions has frequently resulted in their being grouped together under the designation NO_x, although analytic techniques can distinguish clearly between them. Of the two, NO_2 is the more toxic and irritating compound.

Nitrous oxide (N_2O), a product of natural biologic processes in soil, is ubiquitous. It is not known, however, to be involved in any photochemical smog reactions. Although N_2O is not generally considered to be an air pollutant, it is a principal reactant in upper atmospheric reactions involving the ozone layer.

Nitric oxide is an odorless and colorless gas. It is a major by-product of the combustion process, arising both from the oxidation of molecular nitrogen in the combustion air and of nitrogen compounds bound in the fuel molecule. The amount of NO formed from the oxidation of molecular nitrogen is dependent upon such parameters as peak flame temperature, quantity of combustion air, and gas residence time in the combustion chamber. The amount of NO arising from oxidation of fuel-bound nitrogen does not seem to depend significantly on either the type of nitrogen compound involved or the flame temperature, but instead upon the specific air-to-fuel ratio at various stages in combustion.

Nitrogen dioxide (NO_2) is produced in minor quantities in the combustion process (5 to 10 percent of the total oxides of nitrogen). In terms of significant atmospheric loading in populated areas, NO_2 arises mainly from the conversion of NO to NO_2 by a variety of chemical processes in the atmosphere. Nitrogen dioxide is corrosive and highly oxidizing. Its reddish-orange-brown color arises from its absorption of light over a broad range of visible wavelengths. Because of its strong absorption in this range (and also in the ultraviolet spectrum), NO_2 can cause visibility reduction and affect the spectral distribution of solar radiation in the polluted, lower atmosphere.

Photochemical oxidants are chemical entities of concern because of their detrimental effects on biological systems and on certain materials. They are products formed in the atmosphere by sunlight-driven, chemical reactions that involve hydrocarbons (HC)* and NO_x.

The term "photochemical oxidants" is used here to define those atmospheric pollutants that result from photochemical reactions and are capable of oxidizing neutral iodide ions. Extensive research has unequivocally identified several components of the photochemical oxidants mixture. Thus, oxidants in ambient air are known to consist mainly of ozone, peroxyacetylnitrate (PAN), and NO_2 and are suspected to include also (but in smaller amounts) other peroxyacylnitrates, H_2O_2 alkyl hydroperoxides, HNO_3, nitrous acids, peracids, and ozonides. Collectively, they are measured by potassium iodide procedures and are referred to in this report as "oxidants." An important distinction to be made here is that the formation of NO_2 in ambient air clearly precedes the formation of the other oxidants. The relative levels of NO_2 and of the aggregate of the other oxidants vary considerably during the day, with NO_2 invariably being the dominant oxidant earlier in the day. Because of the difference in the variation pattern and in effects between NO_2 and the aggregate of the other oxidants, the NO_2 pollution problem has usually been treated independently of the other photochemical oxidant problems. Furthermore, because of its predominance among the oxidants other than NO_2, ozone has been singled out and treated as the sole representative of such oxidants and has received most of the research attention.

Photochemical air pollution is customarily defined in terms of the concentrations of ozone and NO_2 only. This should not be interpreted to suggest that other photochemical pollutants are thought to be of less concern. Rather, it reflects (1) the fact that ozone and NO_2 pollution problems are more easily quantified and hence are more amenable to research than problems associated with the other pollutants (e.g., eye irritation and visibility reduction) and (2) the assumption that abatement of the ozone and NO_2 pollution problems will, in all probability, alleviate the other photochemical pollution problems.

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* The term "hydrocarbon" is meant to include also all nonhydrocarbon organic compounds capable of participating in the atmospheric oxidant formation process. Accordingly, the terms "hydrocarbons" and "organics" are often used interchangeably.

The ozone found in the lower levels of the Earth's atmosphere has been traced to both natural and anthropogenic sources. One natural source of tropospheric ozone is the ozone present in abundance in the stratosphere that can be transported into the biosphere. Ozone can also form naturally from electrical discharges in the atmosphere and from atmospheric photochemical reactions involving naturally emitted organic vapors and NO_x.

Ozone and other oxidants from anthropogenic sources are products of atmospheric photochemical reactions involving primary organic and inorganic pollutants and atmospheric oxygen. More specifically, the oxidant formation process is initiated by the photolysis of light-absorbing air contaminants such as NO_2, aldehydes, and ozone, resulting in the formation of highly reactive radicals that react subsequently with organic pollutants. The net result of this photochemical activity is the accumulation of ozone, and other oxidants, to concentrations that depend on many factors, including local meteorological conditions (sunlight intensity, air stagnation, temperature, etc.) as well as the concentrations, makeup, and variation patterns of the primary pollutants present. Such dependence of oxidant formation on multiple factors makes this pollution problem immensely complex.

Acidic deposition may involve all of the foregoing pollutants in one manner or another. Sulfur oxides and nitrogen oxides are the precursors of H_2SO_4 and HNO_3, whose formation in the atmosphere may involve particulate sulfate and nitrate and oxidizing agents such as ozone. Since water readily absorbs many gases, or is itself adsorbed onto particles, precipitation serves as an effective scavenging process for the removal of airborne pollutants. In the case of H_2SO_4 and HNO_3, the result is sometimes described as "acid rain." However, acidic gases and particles may impinge directly on the land in the form of dry deposition. Acidic deposition therefore includes dry as well as wet forms.

Although it is difficult to say with certainty whether there has been a historical trend toward increasingly acidic deposition, it is clear that many areas of the world do now experience acidic deposition in the form of acidic precipitation.

Even unpolluted rainfall may be somewhat acidic because of the natural presence of carbon dioxide in the atmosphere. Carbon dioxide dissolves in water to form carbonic acid, a weak acid that shifts the pH value of rain to 5.6 (Barrett and Brodin, 1975). Thus, pH 5.6 provides a convenient reference point for discussing the degree to which precipitation has been altered by man's activities. Of course, the chemistry of precipitation can be influenced by many factors apart from manmade pollution, including sea spray, soil dust, volcanoes, and lightning. The question of concern is whether these natural influences have been or are being overshadowed by anthropogenic sources of pollution. Another way of stating the fundamental issue is: has there been a significant change in the environment as a result of human practices?

Since 1900 there has been an approximately exponential increase in the consumption of gas and oil in this country (see Figure 1-2). Although the total consumption of coal has not increased greatly since about 1925, the consumption of oil and gas has continued to rise precipitously, thus overshadowing coal as the dominant fuel source during the past 50 years. Within

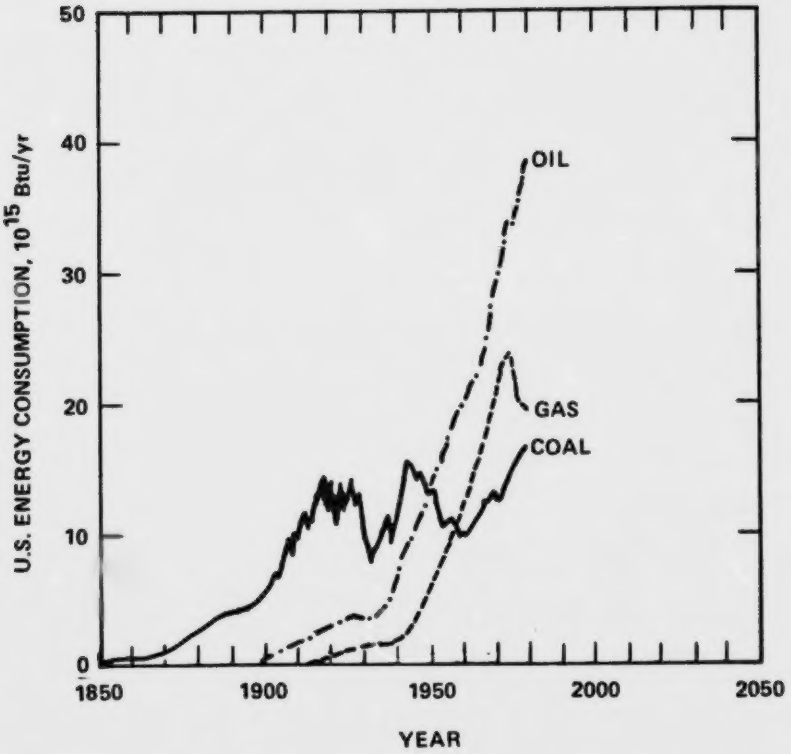


Figure 1-2. Historical patterns of fossil fuel consumption in the United States

Source: Adapted from Hubbert (1976).

this overall increase in fossil-fuel use, however, there have been shifts in the pattern of consumption. Whereas a considerable proportion of coal was formerly used for transportation and heating, oil and gas have since taken over these functions, and now coal is predominantly devoted to electric power generation (Figure 1-3). In fact, electric power generation is the primary factor accounting for an absolute increase in coal consumption over the past two decades. (The decline in coal use in the 1930s was due to the general economic depression, and the decline in the 1950s was due to the availability of relatively inexpensive oil and gas.)

These changes in the pattern of fuel use have been accompanied by changes in the pattern of pollutant emissions. Figure 1-4 illustrates the rise since 1940 in emissions of sulfur and nitrogen oxides, the primary gaseous pollutants resulting from the combustion of fossil fuels. Although there has been a net increase in both categories, the more consistent rise has been in emissions of nitrogen oxides. Almost all (93 percent) emissions of sulfur oxides in the United States arise from stationary point sources, principally industrial and power plant stacks. Nitrogen oxide pollutants, on the other hand, originate about equally from transportation (mobile) sources and from stationary sources, which include not only industrial and power plants, but residential and institutional heating equipment as well (Office of Air Quality Planning and Standards, 1978).

The significance of the difference in these types of sources is that industrial and power plant smokestacks emit their effluents higher into the atmosphere than do vehicles or most space-heating equipment. In fact, there has been a trend since the 1960s toward building tallerstacks as a means of dispersing pollutants and thereby reducing pollutant concentrations in the vicinity of power plants, smelters, and similar sources (Grennard and Ross, 1974).

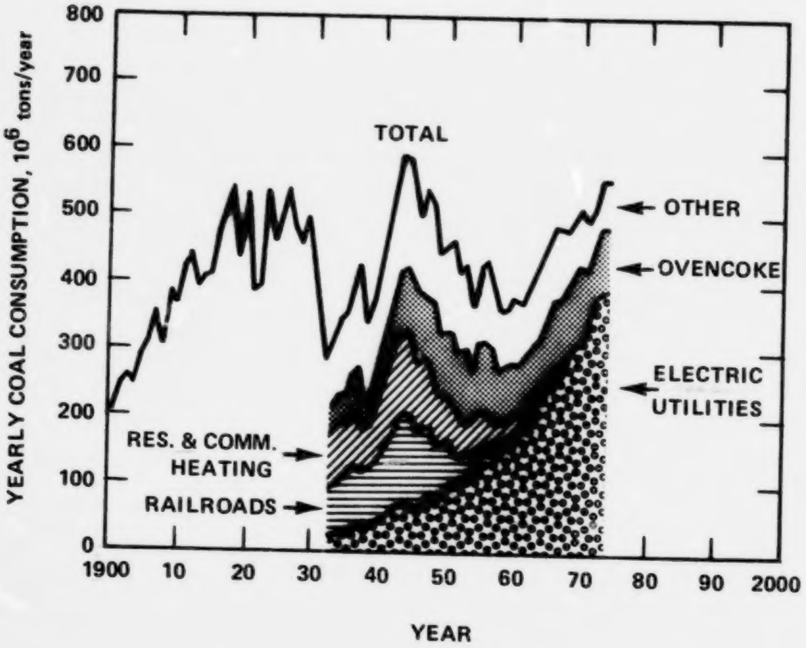
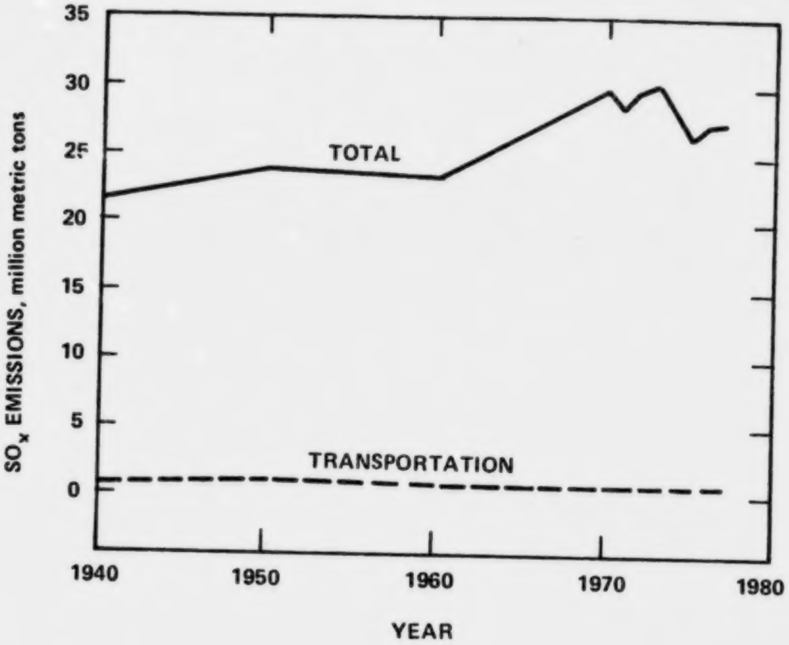


Figure 1-3. Forms of coal usage in the United States. Electric power generation is currently the primary user of coal. (Data from U.S. Bureau of Mines, Minerals Yearbooks 1933–1974).

Source: U.S. Bureau of Mines (1954, 1976).



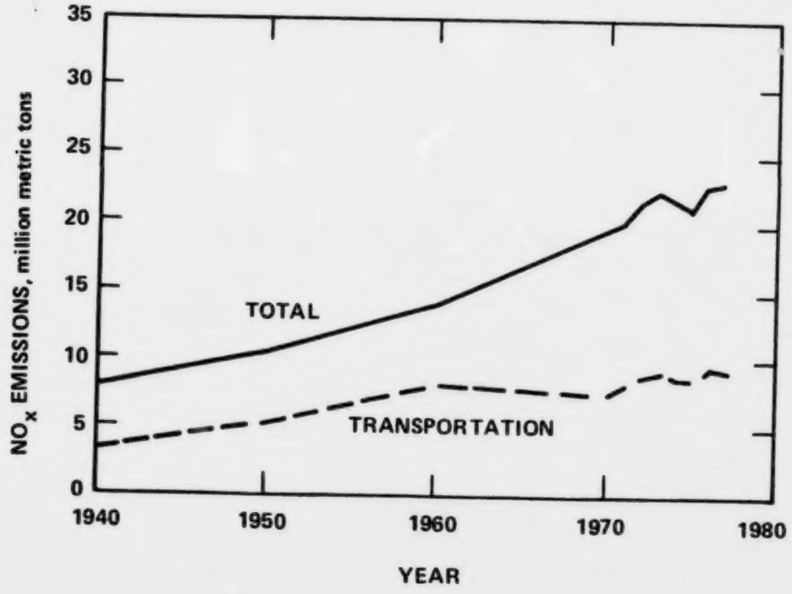


Figure 1-4a. **Trends in emissions of sulfur dioxides.**

Figure 1-4b. **Trends in emissions of nitrogen oxides.**

Source: Office of Air Quality Planning and Standards (1978).

The result has been that sulfur and nitrogen oxides are carried greater distances through the atmosphere by prevailing winds and diffused over larger areas.

Concomitantly, long-range transport allows greater time for chemical reactions to convert these pollutant gases into the components of acidic precipitation (Prahm et al., 1976; Eliassen and Saltbones, 1975; Smith and Jeffrey, 1975). When these gases -- principally SO_2 and various oxides of nitrogen -- combine with water and oxygen in the atmosphere, they form sulfuric acid H_2SO_4 and nitric acid HNO_3.

The mechanisms of these chemical reactions are quite complex and depend on a host of variables ranging from physical properties of the pollutants to weather conditions and the presence of catalytic or interacting agents (Fisher, 1978). Although these processes of atmospheric chemistry are not well understood, it does appear that the long-range transport of sulfur compounds can cover 1000 to 2000 km over three to five days (Pack et al., 1978; Husar and Husar, 1978). Thus, the impact of sulfur pollutants in the form of acidic precipitation may be far removed from their points of origin. It is not yet clear whether the atmospheric transport of nitrogen oxide pollutants is comparable to that of sulfur compounds (Pack, 1978), but nitrates are currently thought to contribute 15 to 30 percent of the acidity of polluted precipitation, with the figure increasing over the past few years and expected to increase further (National Academy of Sciences, 1978a).

2. ECOSYSTEM DYNAMICS

An extremely close mutual relationship that involves the continuing exchange of nutrients and energy, exists between the chemistries of living organisms and their environments processes that have developed over millions of years. Any change in the amount or rate of nutrients or in the flow of energy or both, between living organisms and their environment will cause the biological communities to respond to the changing environment. Adaptation usually occurs, however, except under extreme conditions.

Life depends on the movement of energy and minerals through the biosphere, that thin layer of life-supporting materials surrounding the Earth. The living systems (forests, grasslands, cultivated fields, lakes, rivers, estuaries, and oceans) within the biosphere obtain energy from the sun, nutrients from the Earth's crust (the lithosphere), gases from the atmosphere, and water from the hydrosphere. All of the living systems are interdependent. Energy and nutrients move from one to another. The living systems, together with their physical environments, the lithosphere, hydrosphere, and atmosphere make up the biosphere that is the planet Earth (Smith, 1980; Billings, 1978; Boughey, 1971; Odum, 1971).

Ecosystems are composed of biotic (living) and abiotic (nonliving) components. The biotic component consists of: 1) producers, green plants that capture the energy of the sun; 2) consumers that utilize as their energy source the food stored by the producers and 3) decomposers who obtain their energy by breaking down and converting dead organic matter into inorganic compounds. (See Table 2-1). The abiotic components are air, water, the soil matrix, sediment, particulate matter, dissolved organic matter, nutrients in aquatic systems, and dead or inactive organic matter in terrestrial systems (see Table 2-1) (Smith, 1980; Billings, 1978; Boughey, 1971).

Ecosystems are basically energy processing systems "whose components have evolved together over a long period of time. The boundaries of the system are determined by the environment, that is, by what forms of life can be sustained by the environmental conditions of a particular region. Plant and animal populations within the system represent the objects through which the system functions." (Smith, 1980).

Ecosystems are open systems. They receive from and contribute to the environment that surrounds them. The environment contributes gases, minerals, and energy. Ecosystems utilize these substances and, in turn, make their own contributions to the environment. Energy flows through the system unidirectionally while water, gases, and other minerals are recycled and fed back into the system. The functioning of ecosystems is greatly influenced by the extent to which the gases and minerals are fed back into the system. When materials are not returned to an ecosystem through recycling, they must be obtained in another way. The organismal populations are the structural elements of the ecosystem through which energy flows and nutrients are cycled (Smith, 1980; Billings, 1978; Odum, 1971).

Energy from the sun is the driving force in most ecosystems. Without it, all ecosystems would cease to function. The energy of the sun is captured by green plants through the process of photosynthesis and stored in plant tissues. This stored energy is passed along through ecosystems by a series of feeding steps, known as food webs, in which organisms eat and are eaten. Energy flows through ecosystems in two major food webs, the grazing food web and the detrital food web. The amount of energy that passes through the two food webs varies

TABLE 2-1. COMPOSITION OF ECOSYSTEMS

Component	Description
Biotic (biological):	
Individuals	Plants, animals (man), and microorganisms. These are either producers, consumers, or decomposers.
Producers	Green plants.
Consumers	Herbivores, carnivores.
Decomposers	Macroorganisms (mites, earthworms, millipedes, and slugs) and microorganisms (bacteria and fungi).
Populations	Groups of interbreeding organisms of the same kind, producers, consumers or decomposers, occupying a particular habitat.
Communities	Interacting populations linked together by their responses to a common environment.
Abiotic (physical):	
Atmosphere	Cosmic radiation, temperature, thermal radiation, radioactivity including fallout.
	Water vapor, cloud and precipitation.
	Gases, pressure and wind, Heat and temperature, Fire and pollutants
Lithosphere	Rock and soil particles
	Minerals, water, Radioactivity, heat and temperature, gases Topography
Earth mass	Gravity

Adapted from Billings (1978).

from community to community. The detrital food chain is dominant in most terrestrial and shallow-water ecosystems. The grazing food chain may be dominant in deep-water aquatic ecosystems (Smith, 1980). The two fundamental processes involved in these two food chains are (1) photosynthesis, the capture of energy from the sun by green plants and (2) decomposition, the final dissipation of energy and the reduction of organic matter into inorganic nutrients.

In addition to the flow of energy, the existence of the living world depends upon the circulation of nutrients through the ecosystems. Both energy and nutrients move through the ecosystem as organic matter. It is not possible to separate one from the other. Both influence the abundance of organisms, metabolic rate at which they live, and the complexity and structure of the ecosystem (Smith, 1980). Nutrients, unlike energy, after moving from the living to the nonliving components, return to the living components of the ecosystem in a perpetual cycle. It is through the cycling of nutrients that plants and animals obtain the minerals necessary for their existence.

The gaseous and sedimentary cycles are the two basic types of nutrient or biogeochemical cycles. The gaseous cycles involve carbon, oxygen, and nitrogen. Water, also, is sometimes considered as belonging to the gaseous cycle. In the gaseous cycles, the main nutrient reservoirs are the atmosphere and the ocean. In the sedimentary cycle, to which phosphorus belongs, the reservoir is the soil and rocks of the earth's crust. The sulfur cycle (Figure 2-1), a combination of the two cycles, has reservoirs in both the atmosphere and earth's crust.

Nitrogen, sulfur and water cycles are involved in acidic deposition. Nitrogen, through the agency of microorganisms (bacteria and blue-green algae), moves from the atmosphere to the soil and back (see Figure 2-2). Human intrusions

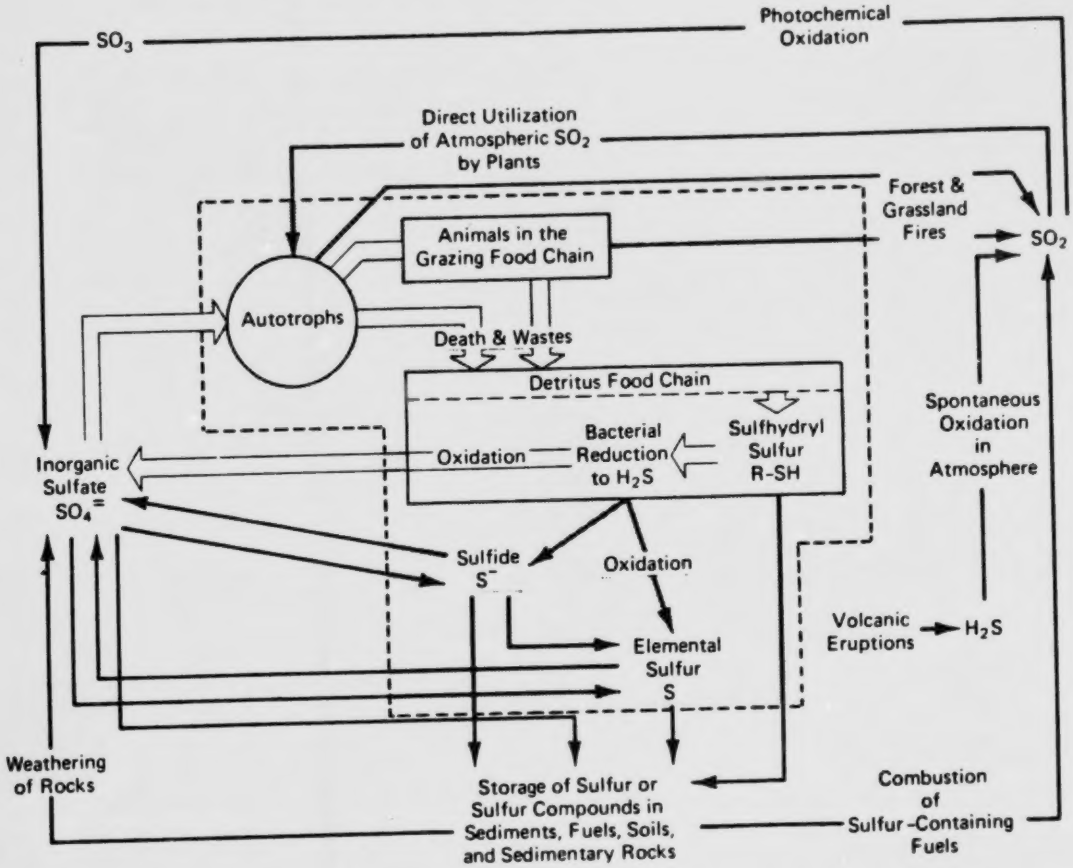

SO$_3$
Photochemical Oxidation
Direct Utilization of Atmospheric SO$_2$ by Plants
Forest & Grassland Fires
SO$_2$
Animals in the Grazing Food Chain
Autotrophs
Death & Wastes
Detritus Food Chain
Bacterial Reduction to H$_2$S
Sulfhydryl Sulfur R-SH
Oxidation
Inorganic Sulfate SO$_4^=$
Spontaneous Oxidation in Atmosphere
Sulfide S$^-$
Oxidation
Elemental Sulfur S
Volcanic Eruptions
H$_2$S
Weathering of Rocks
Storage of Sulfur or Sulfur Compounds in Sediments, Fuels, Soils, and Sedimentary Rocks
Combustion of Sulfur-Containing Fuels

Figure 2-1. **The sulfur cycle (organic phase bounded by dashed line).**

Source: Clapham (1973).

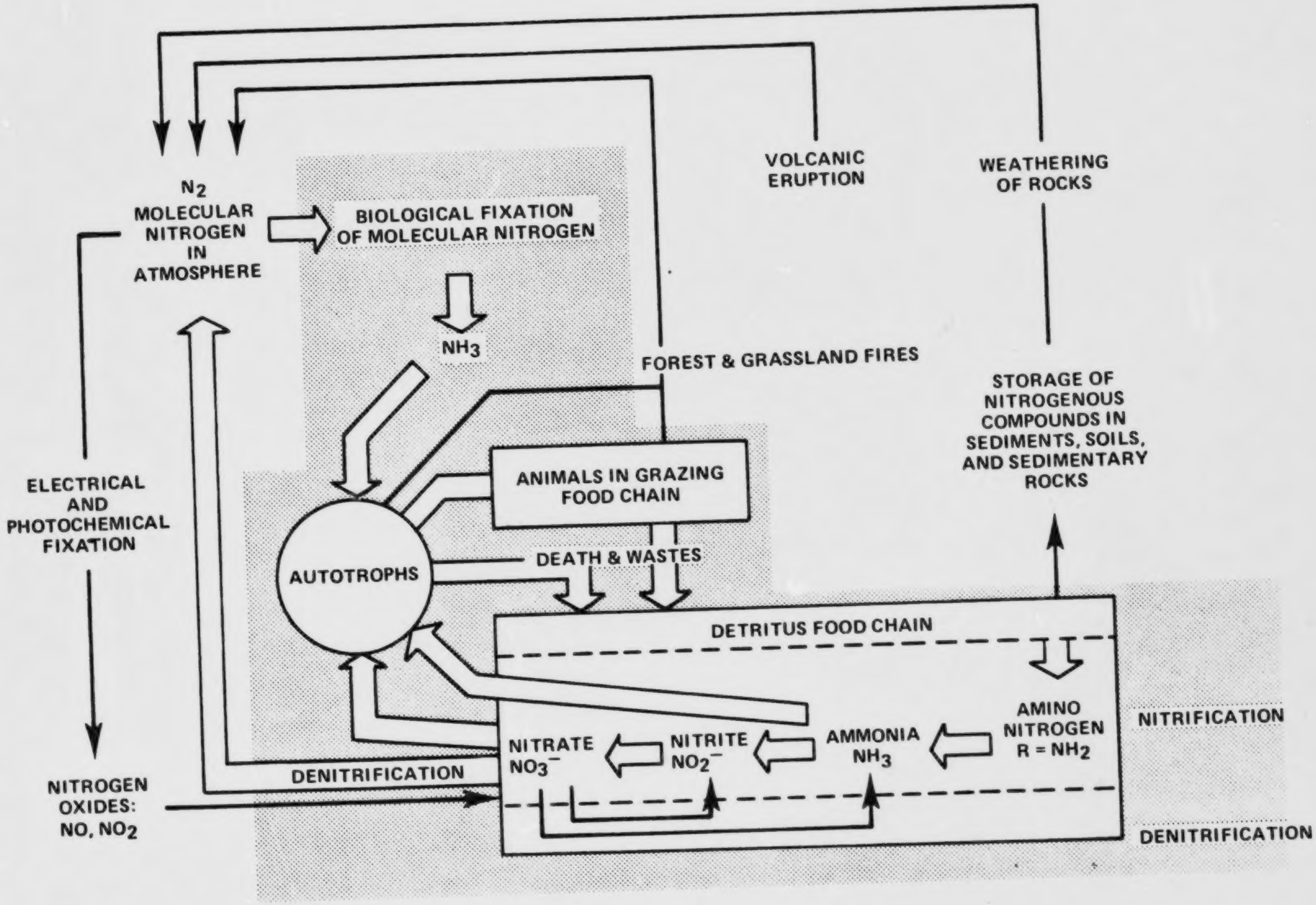


Figure 2-2. The nitrogen cycle. Organic phase shaded.

into the nitrogen cycles include the addition of nitrogen oxides to the atmosphere and ammonia and nitrates to aquatic ecosystems. Sulfur enters the atmosphere from volcanic eruptions, weathering, the surface of the ocean, gases released in the decomposition processes, and combustion of fossil fuels. There is no way to harness or use energy without creating an environmental impact. Both the nitrogen and sulfur cycles have been overloaded in some parts of the world by the combustion of fossil fuels by man. For these cycles to function, an ecosystem must possess a number of structured relationships among its components. By changing the amounts of nitrogen and sulfur moving through the cycles, humans have perturbed or upset the structured relationships that have existed for thousands of years and altered the amounts and the movement of the elements through the ecosystems. The pathways that the elements take through the system depend upon the interaction of the populations and their relationships to each other.

Change is one of the basic characteristics of our environment: weather changes from day to day, temperatures rise and fall, rains come and go, soils erode, volcanoes erupt, and winds blow across the land. These are natural phenomena. Significant environmental changes (perturbations) also result when human beings clear forests, build cities and factories, and dam rivers. All of these environmental changes influence the organisms that live in the ecosystems where the changes are occurring (Moran et al., 1980).

Existing studies indicate that changes occurring within ecosystems, in response to pollution or other disturbances, follow definite patterns that are similar even in different ecosystems. It is possible, therefore, to predict the basic biotic responses of an ecosystem to disturbances such as those caused by environmental stress (Woodwell, 1970; Odum, 1965; Woodwell, 1962). These responses to disturbance are (1) removal of sensitive species and subspecies due to differential kill; (2) reduction in the number of plants and animals (standing crop); (3) inhibition of growth or reduction in productivity; (4) disruption of food chains; (5) return to a previous (e.g. simpler) state of development; and (6) modification in the rates of nutrient cycling.

Ecosystems can respond to environmental changes or perturbations only through the response of the populations of organisms of which they are composed (Smith, 1980). Species sensitive to environmental changes are removed. Therefore, the capacity of an ecosystem to maintain internal stability is determined by the ability of individual organisms to adjust their physiology or behavior to change. The success with which an organism copes with environmental changes is determined by its ability to produce reproducing offspring. The size and success of a population depends upon the collective ability of organisms to reproduce and maintain their numbers in a particular environment. Those organisms that adapt best contribute most to future generations because they have the greatest number of progeny in the population (Smith, 1980; Billings, 1978; Odum, 1971; Woodwell, 1970).

The capacity of organisms to withstand injury from weather extremes, pesticides, acidic deposition, or polluted air follows the principle of limiting factors (Moran et al., 1980; Smith, 1980; Billings, 1978; Odum, 1971). According to this principle, for each physical factor in the environment there exists for each organism a minimum and a maximum limit beyond which no members of a particular species can survive. Either too much or too little of a factor such as heat, light, water, or minerals (even though they are necessary for life) can jeopardize the survival of an individual and, in extreme cases, a species (Smith, 1980; Billings, 1978; Boughey, 1971; Odum, 1971). The range of tolerance (see Figure 2-3) of an organism may be broad for one factor and narrow for another. The tolerance limit for each species

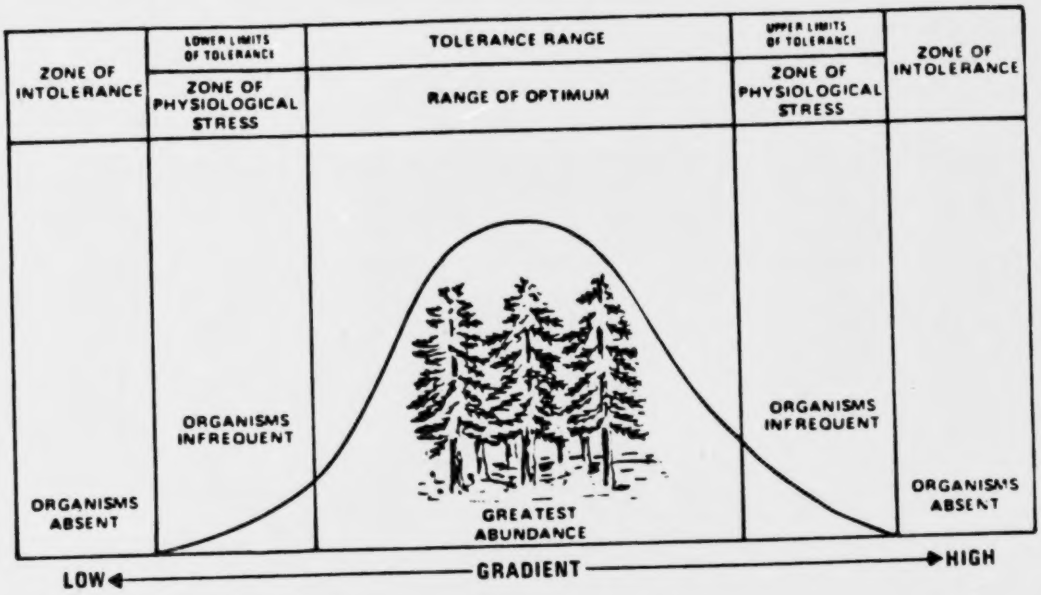


Figure 2-3. Law of tolerance.

Source: Adapted from Smith (1980).

is determined by its genetic makeup and varies from species to species for the same reason. The range of tolerance also varies depending on the age, stage of growth, or growth form of an organism. Limiting factors are, therefore, those which, when scarce or overabundant, limit the growth, reproduction, and/or distribution of an organism (Smith, 1980; Moran et al., 1980; Billings, 1978; Boughey, 1971; Odum, 1971). Acidity of water in lakes and streams is such a factor; e.g., the increasing acidity of many lakes in the northeastern United States has exceeded the range of tolerance for their fish populations.

Organisms can exist only within their range of tolerance. Some populations of organisms, annual plants, insects, and mice, for example, respond rapidly to environmental change. They increase in numbers under favorable conditions and decline rapidly when conditions are unfavorable. Populations of other organisms, such as trees and wolves, fluctuate less in response to favorable or unfavorable conditions by showing little variation in the rates of reproduction and death. Adaptation is the ability of an organism to conform to its environment. Ecosystem stability ultimately is based on the adaptability of the organisms that compose it. Stability may be associated with the ability of a system to return to an equilibrium state after a temporary disturbance (Holling, 1973; May, 1973). The less it varies from and the faster it returns to its original state, the more stable the system (Smith, 1980). Stability also involves persistence, the ability of the populations of an ecosystem to persist through time. Persistence involves resilience, the ability of an ecosystem to absorb changes. Although individual populations within a system may fluctuate greatly in response to environmental changes, the system may be highly resilient (Smith, 1980; Holling, 1973). Contrasted with resilience is resistance, the ability of a system, because of its structure, to resist changes from disturbances. Typically, the most resistant ecosystems have large living components, trees for example, and store nutrients and energy in the standing biomass. Resistant systems, such as forests, once highly disturbed are very slow in returning to their original state (Smith, 1980).

Aquatic ecosystems that lack components in which energy and nutrients may be stored for long periods of time usually are not very resistant to environmental changes (Smith, 1980). For example, an influx of pollutants, such as effluents from sewage, disrupts the system because more nutrients enter the system than it can handle. However, since the nutrients are not retained or recycled within the system it returns to its original state in a relatively short time after the perturbation is removed.

No barriers exist between the various environmental factors, or between an organism or biotic community and its environment. Because an ecosystem is a complex of interacting components, if one factor is changed, almost all will change eventually. "The ecosystem reacts as a whole. It is practically impossible to wall off a single factor or organism in nature and control it at will without affecting the rest of the ecosystem. Any change no matter how small is reflected in some way throughout the ecosystem: no 'walls' have yet been discovered that prevent these interactions from taking place" (Billings, 1978).

Continued or severe perturbation of an ecosystem can overcome its resistance or prevent its recovery with the result that the original ecosystem will be replaced by a new system.

Evaluating the contribution of functioning natural ecosystems to human welfare is a very complex task and usually involves weighing both economic and human social values. However, because natural ecosystems are life support systems, their values should not be quantified in economic terms.

With the passage of time, man has destroyed many of the naturally occurring ecosystems of which he was a part and has replaced them with simplified ecosystems wholly dependent on his care and protection and requiring a large input of energy (Smith, 1980).

3. EFFECTS OF OZONE ON TERRESTRIAL ECOSYSTEMS

3.1 EFFECTS OF OZONE ON AGROECOSYSTEMS

3.1.1 Introduction

Man favors the simple, unstable, and synthetic ecosystems, because when they are extensively managed and subsidized by the use of fossil fuels, they are highly productive. Productivity is the rate at which energy is stored by the photosynthetic activity of green plants (Boughey, 1971; Smith, 1980). Young and successional ecosystems are more productive because they add biomass (accumulate energy) each year. An agricultural ecosystem (agroecosystem) is an example of such a simplified ecosystem. Urban ecosystems, with their cultivated trees, shrubs, grasses, and flowers, are also examples of ecosystems simplified by man. The structural simplicity of these ecosystems (in many cases monocultures) makes them less resistant to environmental and disease stresses or to perturbations such as oxidant pollution. The greater diversity of a mature ecosystem retards the disruption of normal structure and function caused by any type of perturbation. For example, a forest ecosystem in which the communities are composed of many species would show less immediate damage by stress than successional stages having only a few species. Even greater damage would be anticipated in an agroecosystem, which may be considered the simplest of successional stages since often only a single producer species is present.

Agroecosystems and their plant components, because of their greater simplicity and readily visible economic value to humanity, have been studied much more extensively than natural ecosystems. The sections that follow, therefore, deal more extensively with the effects of pollutants on crops and cultivated plants than with the effects on natural ecosystems.

Oxidant injury to vegetation was first identified in 1944 in the Los Angeles Basin. Our understanding of oxidant effects and of the widespread nature of their occurrence has increased steadily since then. Although the major phytotoxic components of the photochemical oxidant complex are ozone and PAN, some data suggest that other phytotoxicants are also present. The peroxyacylnitrates are the most phytotoxic of the known photochemical oxidants; however, the ubiquitous nature of ozone and its association with widespread injury to vegetation make it the most important phytotoxic component of the photochemical oxidant complex.

The effects of photochemical oxidants on vascular plants can be envisioned as occurring at several levels, ranging from the subcellular to the organismal, depending on the concentration and duration of exposure to the pollutant, and on the elapsed time after exposure that effects are observed.

The earliest effect is an increase in cell membrane permeability. Cellular and biochemical changes are ultimately expressed on the organismic level in visible foliar injury, increased leaf drop, reduced plant vigor, reduced plant growth, and death. In the final analysis, biochemical modifications on an individual plant level are manifested by changes in plant communities and then in whole ecosystems (Tingey, 1977).

Leaf stomata are the principal plant entry sites for ozone, PAN, and other phytotoxic air pollutants. Injury only appears when sufficient concentrations of a gas diffuse into the leaf interior and pass into the liquid phase of cells. The response of vascular plants to oxidants may be viewed as the culmination of a sequence of physical, biochemical, and physiological events.

3.1.2 Factors Affecting Plant Response

The response of plants to NO_x, ozone, PAN, or any environmental stress is conditioned by complex, interacting internal and external factors. These include climate and soil factors, interactions among atmospheric pollutants, genetic variability (both between and within species) of plants, and age or stage of growth (Figure 3-1).

Visible injury is identifiable as pigmented, chlorotic, or necrotic foliar patterns. Metabolic cellular disturbances can occur without visible injury and may be reversible. However, most of the growth effects reported until recently were associated with visible injury.

Classic ozone injury is demonstrated by the upper-surface leaf fleck on tobacco and the leaf stipple of grape. Many plants show an upper-surface response with no associated injury to the lower surface of leaves. However, in monocotyledonous plants such as grasses or cereals, and some nonmonocotyledonous plants, the mesophyll tissue is not divided, and bifacial necrotic spotting (flecking) is a common symptom of ozone injury.

Coniferous trees exhibit different symptoms. Ozone is probably the cause of emergence tipburn in eastern white pine (white pine needle dieback) and chlorotic decline, a needle injury of ponderosa pine.

Classic PAN injury appears as a glaze followed by bronzing of the lower leaf surface of many plants. Complete collapse of leaf tissue can occur if concentrations are sufficient high. Early leaf senescence and abscission usually follow the chronic response symptoms. Chronic injury patterns generally are not characteristic and may be confused with symptoms caused by biotic diseases, insect infestation, nutritional disorders, or other environmental stresses.

A great deal of research has been done to define the effects of oxidants on plant growth and yield more accurately. Studies comparing the growth of plants in filtered and nonfiltered field chambers using oxidants in the ambient air have reported up to 50-percent decreases in citrus yield (orange and lemon); 10 to 15 percent supression in grape yield in the first year, and 50

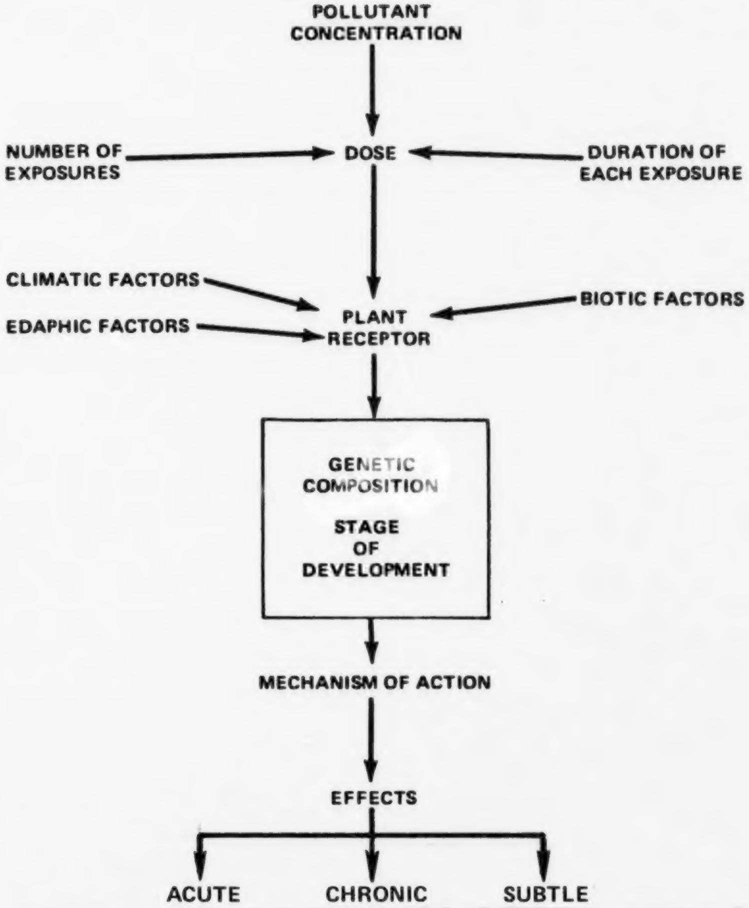


Figure 3-1. Conceptual model of factors involved in air pollution effects on vegetation (modified from van Haut and Stratmann).

to 60 percent reduction over the following 2 years; and a 5 to 29 percent decrease in yield of cotton lint and seed in California. Losses of 50 percent in some sensitive potato, tobacco, and soybean cultivars have been reported in the eastern United States. It is apparent that oxidants in the ambient air reduce yields of many sensitive plant cultivars.

Experimental chambers with controlled environments have been used to study both short-term and long-term effects of exposure to ozone. Multiple acute exposures (785 $\mu g/m^3$, or 0.40 ppm) of radishes for 1.5 hr resulted in reductions in root growth (Tingey et al., 1973a). The reductions in root growth from the multiple ozone exposures were equal to additive effects of three single exposures. When soybean plants were exposed to 1468 $\mu g/m^3$ (0.75 ppm) ozone for 1 hr, root growth was consistently reduced more than top growth. There was also a reduction in nodule weight and number. The greater reduction of root growth than top growth is related to the transport of the products of photosynthesis. Ozone also affects the process of nitrogen fixation in clover, soybean, and pinto bean through reduction in nodule number, but neither nodule size nor efficiency of nitrogen fixation is influenced. The effect of ozone on the nitrogen fixation process in legumes, if widespread, could have a major impact on plant communities and affect fertilizer requirements. There are indications that the effect of ozone on nodulation may be related to carbohydrate supply in host plants (Tingey and Blum, 1973).

Experimental long-term exposures of a variety of crops as well as ornamental and native plants to ozone have resulted in a reduction in growth and/or yield. Throughout a growing season, 14 species representative of the aspen plant community were exposed to ambient air (98 to 137 $\mu g/m^3$ ozone, or 0.05 and 0.07 ppm) and to ozone (290 and 588 $\mu g/m^3$ or 0.15 and 0.30 ppm) for 3 hr/day, 5 days/week, and to charcoal-filtered air. Foliar injury to all species resulted at the highest pollution concentration (Harward and Treshou, 1975). The growth of two soybean cultivars (Hood and Dare) was inhibited by intermittent exposure to ozone at 196 $\mu g/m^3$ (0.10 ppm) for 3 weeks. Growth of both root and top was decreased. Similar results were noted with radish, except that a lower concentration (98 $\mu g/m^3$ or 0.05 ppm) inhibited growth (Tingey et al., 1973a). In the aforementioned studies, the reduced growth occurred even though there were very few visible symptoms of plant injury.

A reduction of 30 percent in the yield of wheat occurred when, at anthesis, wheat was exposed to ozone at 392 $\mu g/m^3$ (0.2 ppm), 4 hr/day for 7 days (Kochar, 1974). A significant reduction in the yield of tomato was noted when plants were experimentally treated with ozone at 686 $\mu g/m^3$ (0.35 ppm) (Oshima et al., 1975). Lower fruit set and fewer harvested fruit caused the reduction. Chronic exposures to ozone at 98 to 290 $\mu g/m^3$ (0.05 to 0.15 ppm) for 4 to 6 hr/day produced reductions in yield in soybean and corn grown under field conditions. The threshold for measurable effects for ozone appears to be between 98 and 196 $\mu g/m^3$ (0.05 to 0.10 ppm) for sensitive plant cultivars (Heagle et al., 1974). This is well within the range of ozone level monitored in the eastern United States.

Two of the most critical factors in determining plant response to air pollution are duration of exposure and concentration of pollutants. Response may be characterized by a measurable change in any plant function, such as biochemical pathways, gas exchange rates, photosynthetic rates, physiological reactions, degree of visibly recognizable leaf injury, or subsequent growth and yield. Plant responses may be beneficial or detrimental. They may also involve the expression of growth and yield effects without foliar symptoms or may lead to overt symptoms that seldom become more serious than those associated with acute injury or chronic injury.

In interpreting exposure-response studies wherein a measured plant response is correlated with the length of exposure, it is important to realize that the relationship between exposure and the amount of pollutant entering the plant may be influenced significantly by environmental factors which control rates of pollutant flux into plant leaves and by plant factors that determine the metabolic fate of the pollutant within leaf tissues.

The concept of limiting values was used by Jacobson (1977) to define the boundary between doses of a pollutant that are likely to cause measurable foliar injury to vegetation and those that are not. Foliar injury was used as the index of plant response. The ranges for limiting values for effects of ozone are:

1. Trees and shrubs:
   - 400 to 1000 μg/m^3 (0.2 to 0.51 ppm) for 1 hr
   - 200 to 500 μg/m^3 (0.1 to 0.251 ppm) for 2 hr
   - 120 to 340 μg/m^3 (0.06 to 0.17 ppm) for 4 hr
2. Agricultural crops:
   - 400 to 800 μg/m^3 (0.2 to 0.41 ppm) for 0.5 hr
   - 200 to 500 μg/m^3 (0.1 to 0.251 ppm) for 1 hr
   - 75 to 180 μg/m^3 (0.04 to 0.09 ppm) for 4 hr

The range of limiting values for PAN is:

1000 μg/m^3 (0.2 ppm) for 0.5 hr
500 μg/m^3 (0.1 ppm) for 1 hr
175 μg/m^3 (0.035 ppm) for 4 hr

Doses of ozone or PAN greater than the upper limiting values are likely to cause foliar injury.

The data points used to determine the limiting values listed above are not necessarily threshold values but were based on available published research data. More than 200 studies were surveyed. Any limitations that were present in the experimental techniques used in the studies are expressed in the data points. Another constraint of the PAN data is the limited number of studies.

Plant sensitivity to ozone and PAN is conditioned by many factors (Figure 3-1). Genetic diversity in sensitivity to ozone between species and cultivars within a species is well documented (Heck, 1968; Reinert, 1975). Variants in sensitivity to ozone within a natural species are well known for several pine species, including white, loblolly, and ponderosa (Berry, 1971; Davis, 1970). Plant sensitivity to oxidants can be changed by both climatic and edaphic factors. A change in environmental conditions can initiate a change in sensitivity at once, but it will be 3 to 5 days before the response of the plant is totally modified. Plants generally are more sensitive to ozone when grown under short photoperiods, medium light conditions, medium temperature, high humidity, and high soil moisture. Injury from PAN may increase with increasing light intensity (Dugger et al., 1963). Conditions during exposure and growth affect the response of plants to oxidants in similar ways. In general, environmental conditions optimum for plant growth tend to increase the sensitivity to ozone. At the time of exposure, factors that increase water stress tend to make plants more tolerant to ozone. Soil moisture is probably the most important environmental factor that affects plant response to oxidants during the normal growing season (Dean and Davis, 1967; Taylor et al., 1960; Walker and Vickery, 1961). Physiologic age affects the response of the leaf to oxidants. Young leaf tissue is most sensitive to PAN (Bobrov, 1952; Reinert, 1975), whereas newly expanding and maturing tissue is most sensitive to ozone (Macdowall, 1965). Light is required for plant tissue to respond to PAN; a similar light requirement is not needed for plants to respond to ozone.

The majority of effects observed, such as suppression of root growth, mineral uptake, and nitrogen fixation, apparently result from a suppression in photosynthesis and modifications in photosynthate distribution. This suppression in metabolic reserves ultimately slows plant growth and renders the plant more sensitive to other stresses. Physiological changes can provide a sensitive means of monitoring the health and vigor of the plant with or without visual injury. Ozone affects pollen germination in some species and may affect yield through incomplete pollination of flowers. Investigations with *Arabidopsis thaliana* showed no mutagenic effects from ozone over seven generations (Bruton, 1974).

Mixtures of pollutants can cause effects below the levels caused by either gas alone; however, there is some disagreement concerning ozone interactions with other gases. Ratios of gas mixtures, intermittent exposures, sequential exposures to pollutants, and predisposition by one pollutant to the effects of a second pollutant may be important in nature, but insufficient knowledge is available to elucidate the effects.

The response of plants to oxidants may be conditioned by the presence or absence of biotic pathogens. Depending on the plant and the pathogen, oxidants may cause more or less injury to a given species. Oxidant injury to ponderosa pine predisposes the trees to later invasion by bark beetles (Miller et al., 1968; Stark et al., 1968). Ozone and ozone-sulfur dioxide mixtures can decrease the population of some plant-parasitic nematodes. Variable plant responses have been noted when herbicides were used in the presence of high oxidant concentrations.

Little research on the effects of oxidants on ferns, nonvascular green plants, and microorganisms has been reported. Lichens and mosses are responsive to acid gases, but there is no definite evidence that they respond to oxidants. Ferns may be especially sensitive, but their injury response is different from that of higher vascular plants. Growth and sporulation of fungi on surfaces are usually, but not always, affected. Ozone from 0.1 to several milligrams per liter of solution is required to kill many microorganisms in liquid media. Most work with microorganisms has been done to study the effectiveness of ozone as a biocide in the storage of vegetation or treatment of water or sewage supplies.

3.2 EFFECTS OF OZONE ON NATURAL ECOSYSTEMS

3.2.1 Introduction

The stresses placed on the communities and the ecosystems in which they exist can be far-reaching, since the changes that occur may be irreversible. For example, it has been suggested that the arid lands of India are the result of defoliation and elimination of vegetation that induced local climatic changes not conducive to the reestablishment of the original vegetation (Bryson and Wendland, 1970).

Ecosystems tend to change with time, and sequential changes in the types of populations within a community are usually recognizable. Adaptation, adjustment, and evolution are constantly taking place as the biotic component, the populations, and the communities of living organisms interact with the abiotic component in the enviornment. The interaction and exchange of energy and nutrients over time result in sequential or, in some cases, cyclic or telescoped changes in populations and communities.

Diversity and structure are most changed by pollution as a result of the elimination of sensitive species of flora and fauna and the selective removal of the larger overstory plants in favor of plants of small stature (Woodwell, 1970, 1963). The result is a shift from the complex forest community to the less complex, hardy shrub and herb communities. The opening of the forest canopy changes the environmental stresses on the forest floor, causing differential survival and, consequently, changed gene frequencies in subcanopy species.

Associated with the reduction in diversity and structure is a shortening of food chains, a reduction in the total nutrient inventory, and a return to a simpler and less stable successional stage (Woodwell, 1970, 1963). In addition, the pollutants act as predisposing agents, and an increase in the activity of insect pests and certain diseases occurs (Sinclair, 1969; Woodwell, 1970). It should be emphasized that ecosystems are usually subjected to a number of stresses at the same time, not just to a single perturbation.

3.2.2 General Responses of Natural Ecosystems to Stress by Oxidants

Natural ecosystems in California and in the Appalachian Mountains in the eastern United States have suffered from oxidant pollution.

3.2.2.1 The Appalachian Mountains--In the eastern United States, a disease called emergence tipburn, found in eastern white pine, was related to ozone by Berry and Ripperton (1963). The disease is characterized by bands of necrosis initiated in the semimmature tissue of elongating needles and spreading to the needle tip.

Under forest conditions, the affected trees occur randomly in the stand, and the same trees are injured repeatedly in a single season or in successive years (Berry, 1961). Only sensitive genotypes are affected, and these are gradually eliminated. Eastern white pine either forms pure stands or occurs in mixtures with other species in abandoned fields. Under these conditions, it is an important pioneer tree (U.S. Forest Service, 1973). In established stands, it is a major component of 4 forest types and an associate in 14 other types and inhabits a range extending over 7 million acres, from the Lake States to the Appalachian Mountains (U.S. Forest Service, 1973). Berry (1961) reported that post-emergence tipburn occurs throughout the natural range of this species. There is also evidence of a slow decline in tree vigor caused by the deterioration of feeder rootlets. Skelly et al. (1977) in 1975 and 1976 also noted post-emergence acute tipburn on white pine growing at three different sites along the Blue Ridge Parkway.

High concentrations of ozone in the forested areas of the eastern United States cause severe injury to eastern white pine (Berry, 1964; Skelly et al., 1977; U.S. Forest Service, 1973) and other forest species. Berry (1964) reported levels of oxidant as high as 230 µg/m³ (0.12 ppm) at a mountaintop monitoring station in June 1962. An air monitoring network operated by Virginia Polytechnic Institute and State University at three locations (the Blue Ridge Mountains, the Shenandoah Valley, and the southern Appalachians) recorded total oxidant peaks as high as 250 µg/m³ (0.13 ppm) during early July 1975, along with 43 hr of exposure at concentrations of 160 µg/m³ (0.08 ppm) (Skelley et al., 1977). In June 1976, oxidant levels exceeded 160 µg/m³ (0.08 ppm). After these episodes, significant increases in oxidant injury were observed (particularly in the Blue Ridge Mountains) involving three categories of eastern white pine: 1) those previously without symptoms, 2) those with chlorotic mottle, and 3) those exhibiting chlorotic dwarf symptoms. Such incidences suggest the need for more comprehensive studies of oxidant (and SO_2) effects in forests of the eastern United States.

The oxidant peaks mentioned above were related to oxidant transport from urban areas to the northeast.

Studies by Davis and Wood (1972) suggest that other conifer species, in particular, Virginia pine and jack pine, may be more sensitive to ozone than eastern white pine. In addition, there is a synergistic interaction between low concentrations of ozone and sulfur dioxide that is the cause of the chlorotic dwarf disease of eastern white pine (Dochinger et al., 1970). A study by Ellertsen et al. (1972) showed 10 percent mortality between 1956 and 1965 in dominant and codominant eastern white pines near an industrialized area that included several hundred square miles on the Cumberland Plateau. The combined effects of ozone and sulfur dioxide were considered responsible for the tree decline. Because eastern white pine represented only 5 percent of the total wood volume available for harvest, the economic impact was slight. There was no effort to interpret pollutant effects in an ecosystem context. In the long run, the broader question to be addressed regards the effects of pollutant stress on all major ecosystem components, primarily on producers, consumers, and decomposers. An analysis of the multiple effects of oxidants on eastern forest ecosystems will present a much more adequate picture of the effects pollution is having on these forests.

The studies to delineate the effects of oxidant episodes in the Appalachian Mountains are continuing.

3.2.2.2 California--In southern California, the coastal chaparral ecosystem, dominated by chamise and manzanita or by woodland species (including the live oaks and big cone spruce), and the coniferous forest ecosystems have received severe exposure. The desert ecosystems in the vicinity of mountain passes connecting the coastal and desert regions have also undoubtedly been exposed.

Injury has been well documented only in the mixed-conifer forest ecosystem of the San Bernardino Mountains. Early symptoms of injury in conifer species were reported in a number of California national forests in 1970 (Miller and Millecan, 1971). In the southern Sierra Nevada, Forest Service surveys made in 1975 (Williams et al., 1977) have detected increased injury in ponderosa pine at many locations in the Sequoia National Forest, Sequoia

National Park, and Kings Canyon National Park since 1970. Specific stands of mixed conifer forest on the western slopes of the southern Sierra Nevada now appear to be affected by oxidants from the San Joaquin Valley (Miller et al., 1977). The potential loss of timber growth in this area alone is a very serious prospect.

The interaction of pollutant and inversion layers at the heated mountain slope results in the vertical venting of oxidants over the mountain crest by up-slope flow.

Oxidant concentrations ranging from 100 to 200 μg/m^3 (0.05 to 0.10 ppm) at altitudes as high as 2432 m (8000 ft), approximately 1033 m (3400 ft) above the mountain crest, were measured by aircraft.

The total oxidant concentrations have been measured continuously from May through September since 1968 at the Rim Forest/Sky Forest monitoring station. During each of the first 7 years of monitoring, between June and September, the total number of hours with concentrations of 160 μg/m^3 (0.08 ppm) or more of ozone was never less than 1300 hours. The number of hours wherein the total oxidant concentration was 390 μg/m^3 (0.20 ppm) or higher increased from fewer than 100 in 1969 to nearly 400 in 1974. It is not uncommon to observe momentary oxidant peaks as high as 1180 μg/m^3 (0.60 ppm). The duration of oxidant concentrations exceeding 200 μg/m^3 (0.10 ppm) was 9, 13, 9, and 8 hr/day going from the lower to the higher altitude stations.

The transport of the urban plume from the coast northeastward to the mountains can be readily demonstrated. Because of this transport, the permanent vegetation constituting natural ecosystems receives a large chronic exposure, and the short-lived, higher-economic-value vegetation constituting the agroecosystem of the Los Angeles coastal plain is subjected to injurious doses in intermittent, short-term fumigations. Each situation has measurable economic and aesthetic effects, but on different time scales. The single-species agricultural ecologic system (the agroecosystem) has little resilience to pollutant stress; chronic exposures caused disruption of both structure and function in the natural ecosystem that may be irreversible.

3.2.3 Investigating the Effects of Oxidant Stress on Ecosystems

3.2.3.1 Ecosystem Modeling--Ecosystems are very complex and extremely difficult to understand. An approach to understanding these complexities is to describe them in mathematical terms. However, before mathematical shorthand can be used, the components to be studied must be defined and and their interactions and relationships with one another identified. To understand the stresses placed on ecosystems by perturbations such as ozone-oxidant air pollution, those elements that could be particularly vulnerable to pollutants must also be identified. The mathematical and computer capability for modeling ecosystems exists, but ecological science does not yet possess sufficient understanding of all of the interactions at the ecosystem level (Auerbach et al., 1977). Therefore, simulation models of forest ecosystems are extremely scarce (Wiegert, 1975). Modeling of the coniferous forest biome is discussed by Overton (1975), and modeling of the eastern forest biome is treated by O'Neill (1975). The usual modeling approach is to select specific processes such as energy flow and nutrient cycling. These processes are a result of the structural interrelationships existing among the various components (soil, water, nutrients, producers, consumers, and decomposers). (Sinclair, 1969). Energy and nutrients may enter or leave an ecosystem by a variety of pathways. These processes may be described mathematically, and a model may be developed that is an approximation of the real world. This model may then be used to make predictions about the ecosystem. Computer programs for solving the equations explaining interactions of the ecosystem components already exist. Once the model is running smoothly on the computer, it is possible to impose various experimental conditions (e.g., clear cutting or selective cutting) and observe the effects on specific processes such as energy or nutrient flow. Sensitivity analysis can then be performed to determine which transfer coefficients are most sensitive to stress and how much stress is required to cause deterioration of the ecosystem.

No models dealing with oxidant stress on communities or ecosystems exist; however, models do exist that deal in general terms with disturbance, (Levin and Paine, 1976), sensitivity (Botkin and Sobel, 1976; Estberg and Patton, 1976; Innis, 1976; Patten, 1976), and stability (Botkin and Sobel, 1976; Estberg and Patton, 1976; Innis, 1976; Patten, 1976) at community and ecosystem levels. Forest succession has been described by Shugart et al. (1973) and Botkin and Miller (1974). The area occupied per biotic unit over time is very important for defining and predicting long-term successional changes in plant communities as a result of pollutant stress. In view of the trend of increasing oxidant concentrations downwind from urban areas (Blumenthal et al., 1974), a much more precise understanding of chronic effects on both natural ecosystems and agroecosystems is required. Descriptive and predictive models dealing with the responses of biologic systems can provide the best input to the decision models needed for standard setting, land use planning, and resource management.

3.2.3.2 Modeling the Effects of Oxidant Stress on a Western Mixed Conifer Forest Ecosystem--The recent history of the mixed conifer forest of the San Bernardino Mountains has been analyzed (Taylor, 1973). The analysis was conducted by nearly a dozen coinvestigators representing many disciplines (Taylor, 1973). This analysis included and initial inventory of ecosystem components and processes, as indicated in Figures 3-2 through 3-6. The

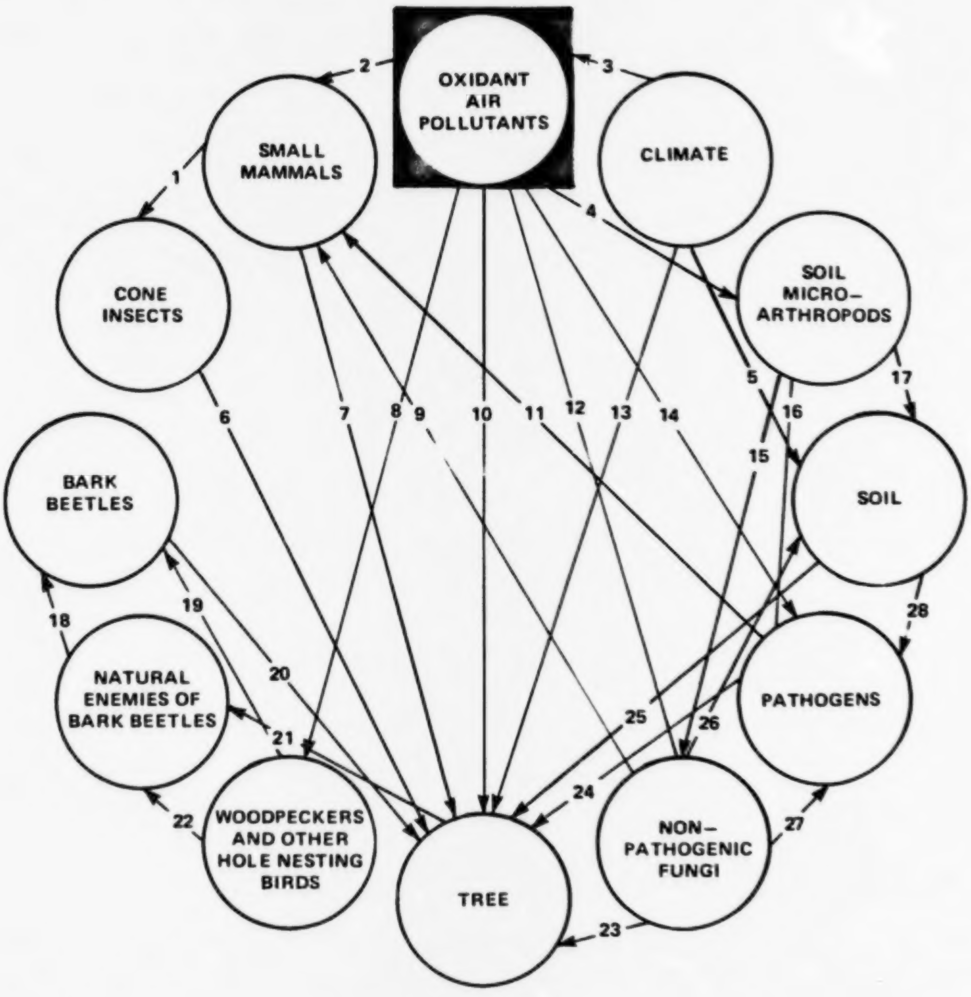


Figure 3-2. Organism-level interactions in a mixed-conifer forest.

1. Competition for food supply
2. Direct effect of ozone on small-mammal physiology
3. Climatic control of oxidant concentration in forest
4. Direct effect of ozone in soil microarthropods
5. Effect of precipitation and temperature on soil moisture and soil temperature
6. Insect damage to developing cones
7. Damage by small mammals to developing cones and importance of cone crop as animal food supply
8. Direct effect of ozone on physiology of cavity-nesting birds
9. Role of fruiting bodies of nonpathogenic fungi in nutrition of small animals
10. Direct effect of ozone on tree physiology
11. Role of fruiting bodies of pathogens in nutrition of small animals
12. Direct effect of ozone on nonpathogenic fungi
13. Effect of temperature and evaporative stress on tree growth
14. Direct effect of ozone on pathogenic fungi
15. Interaction of nonpathogenic fungi and soil microarthropods
16. Interaction of pathogenic fungi and soil microarthropods
17. Effect of soil microarthropods on litter reduction
18. Impact of predation and parasitism on bark beetles
19. Predation of bark beetles by woodpeckers
20. Effect of bark beetles on tree mortality and vigor and effect of phloem thickness and moisture on bark beetles
21. Effect of phloem moisture and thickness on natural enemies of bark beetles
22. Influence of woodpeckers on rate of parasitism
23. Effect of nonpathogenic fungi on tree growth
24. Effect of pathogens on tree vigor and mortality
25. Effect of soil moisture and soil temperature on tree growth
26. Effect of soil moisture and temperature on occurrence of nonpathogenic fungi
27. Interaction of pathogenic and nonpathogenic fungi
28. Effect of soil moisture and temperature on occurrence of pathogenic fungi

Figure 3-2 (continued). Organism-level interactions in a mixed-conifer forest. Types of interactions shown here.

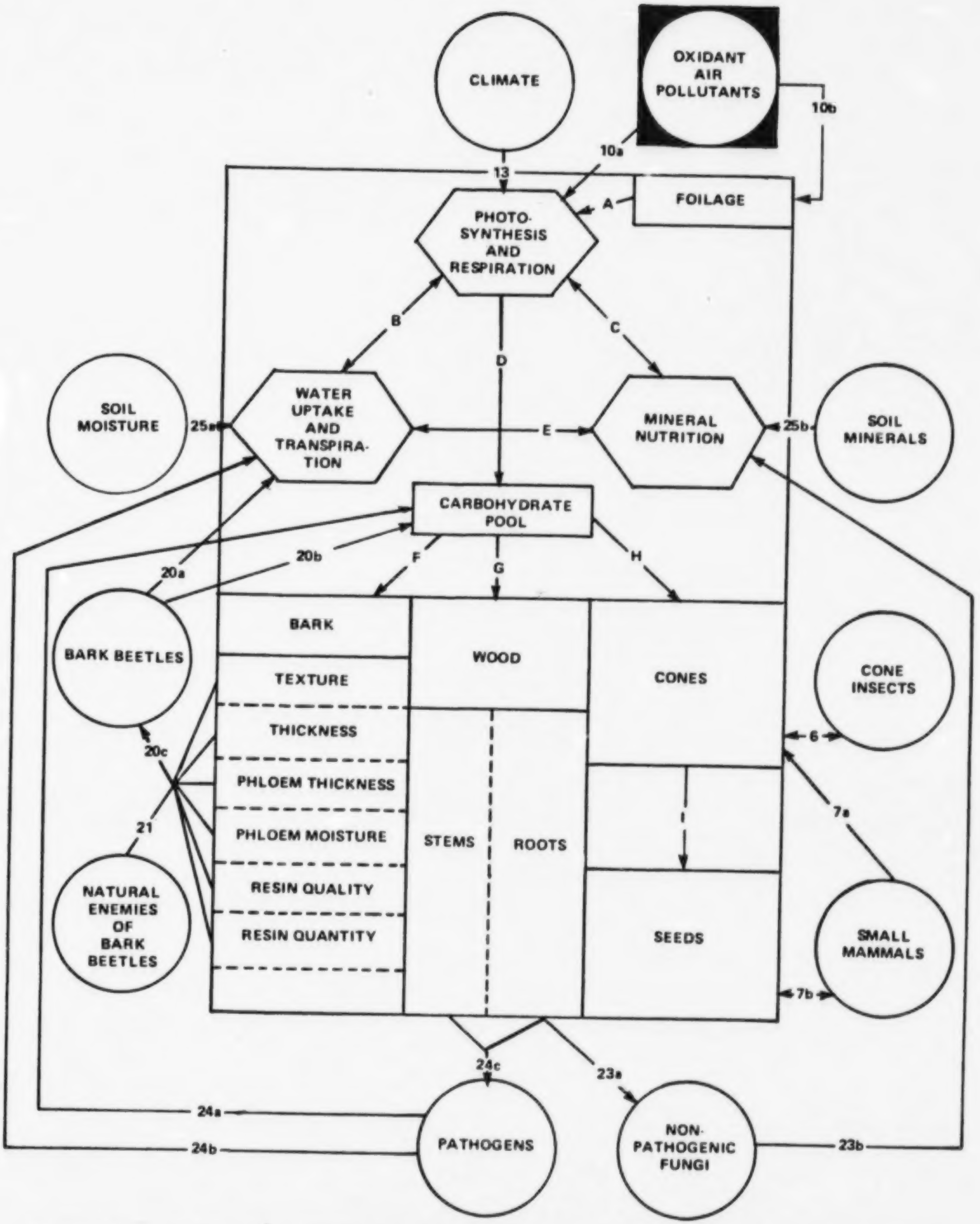


Figure 3-3. Tree-level interactions in a mixed-conifer forest ecosystem (a = direct influence of external factors on trees; b and c = influence of tree condition on external factors).

A.	Relationship between net photosynthesis, foliage age, and foliage retention
B.	Effect of plant moisture stress on net photosynthesis
C.	Relationship between mineral uptake and net photosynthesis
D.	Relationship between net photosynthesis and carbohydrate storage
E.	Relationship between water uptake and mineral nutrition
F.	Relationship between carbohydrate storage and bark characteristics
G.	Relationship between carbohydrate storage and wood production
H.	Relationship between carbohydrate storage and cone production
I.	Relationship between cone crop and seed crop
6.	Cone insect damage to developing cones
7a.	Small-mammal damage to developing cones
7b.	Small-mammal predation of seeds
10a.	Effect of ozone on photosynthesis and respiration
10b.	Effect of ozone on needle retention
13.	Effect of temperature, light intensity, and evaporative stress on photosynthesis and respiration
20a.	Effect of bark beetles on water uptake and transpiration, and relationships of tree moisture stress to bark beetle attack
20b.	Effect of bark beetles on tree carbohydrate concentration and relationships of carbohydrate concentration to bark beetle population in trees
20c.	Relationship between bark beetle characteristics and bark beetle attack and population
21.	Relationship between bark characteristics and natural enemies of bark beetles
23a.	Relationship between root characteristics and mycorrhizal-forming non-pathogenic fungi
23b.	Effect of nonpathogenic fungi on mineral uptake
24a.	Effect of pathogens on tree carbohydrate concentration and relationship of carbohydrate concentrations to pathogen attack
24b.	Effect of pathogens on water uptake and transpiration
24c.	Relationship between stem and root characteristics and pathogen attack
25a.	Effect of soil moisture and temperature on water uptake and transpiration
25b.	Effect of soil mineral concentration and temperature on mineral nutrition of tree

Figure 3-3 (continued). Tree-level interactions in a mixed-conifer forest ecosystem.

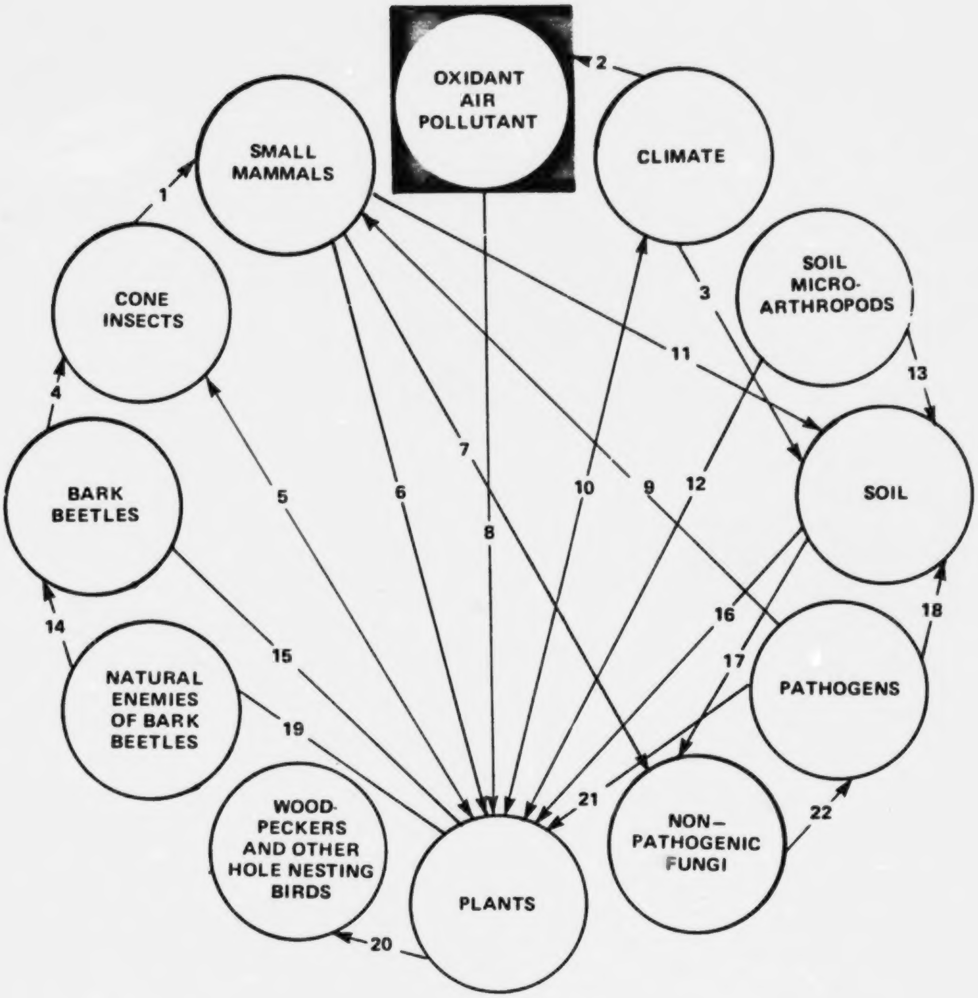


Figure 3-4. Community-level interactions in a mixed-conifer forest ecosystem.

1. Competition between woodpeckers and small mammals
2. Climate control of oxidant concentration in different forest communities
3. Effect of precipitation and temperature on soil moisture and soil temperature in different forest communities
4. Predation of bark beetles by woodpeckers in different forest communities
5. Effect of cone crop abundance on cone insect populations in different forest communities
6. Effect of cone crop abundance on small-mammal populations in different forest communities
7. Fruiting bodies of nonpathogenic fungi as food for small mammals in different forest communities
8. Smog-caused mortality and morbidity in different forest communities
9. Fruiting bodies of pathogens as food for small mammals in different forest communities
10. Effect of temperature and evaporative stress on species composition in different forest communities
11. Relationship between soil characteristics and population density of burrowing small mammals in different communities
12. Relationship between plants and microarthropod population
13. Relationship between soil characteristics and microarthropod population
14. Bark beetle mortality caused by natural enemies in different forest communities
15. Effect of bark beetles on tree mortality and vigor in different forest communities
16. Relationship between soil characteristics and forest community composition and growth
17. Relationship between soil characteristics and species distribution and behavior of nonpathogenic fungi
18. Relationship between soil characteristics and species distribution and behavior of pathogens
19. Influence of forest community type on populations of natural enemies of bark beetles
20. Woodpecker distribution and density in different forest communities
21. Effect of pathogens on tree vigor and mortality in different forest communities
22. Relationship between nonpathogenic fungi and forest community composition and growth

Figure 3-4 (continued). Community-level interactions in a mixed-conifer forest ecosystem.

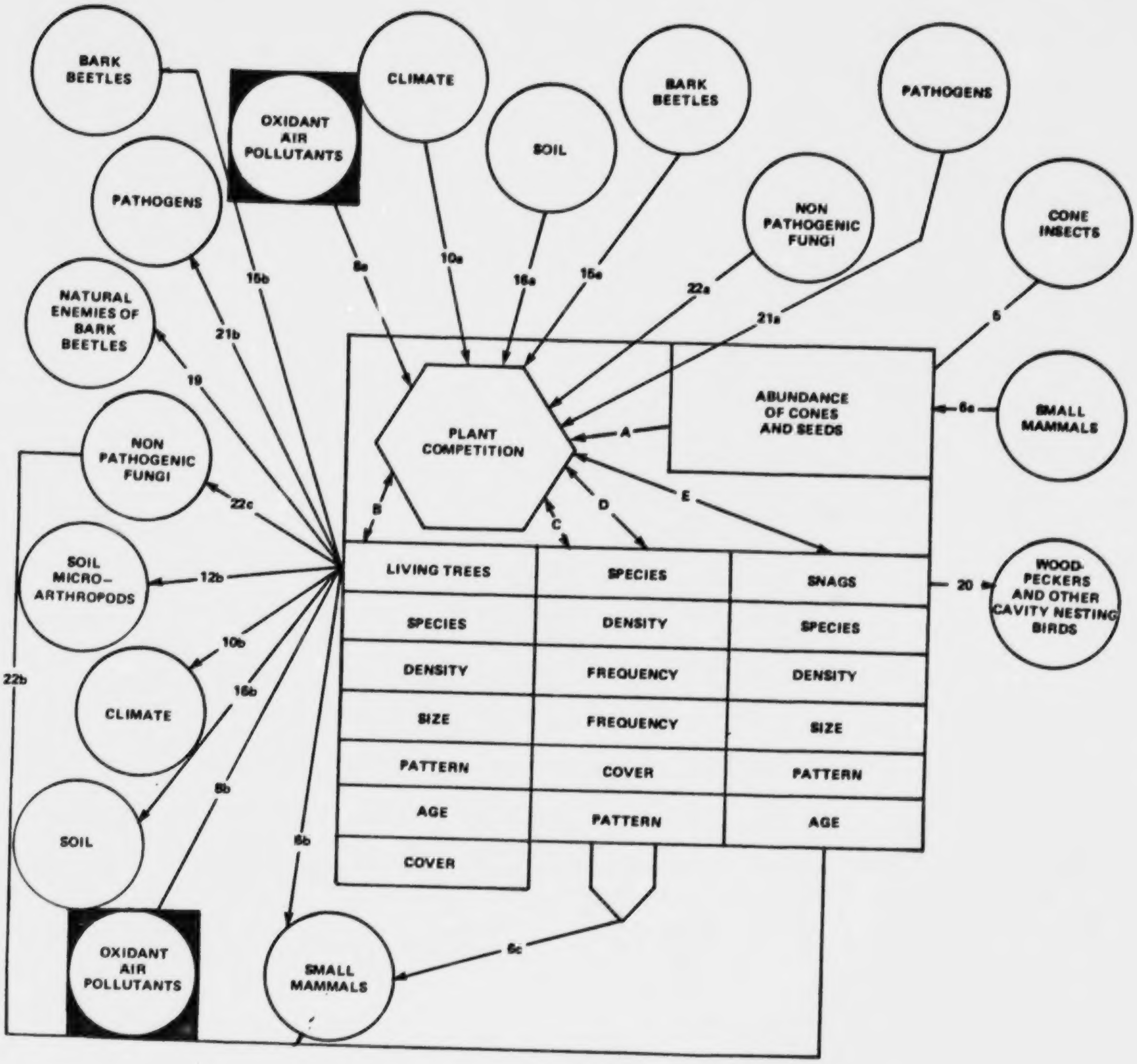
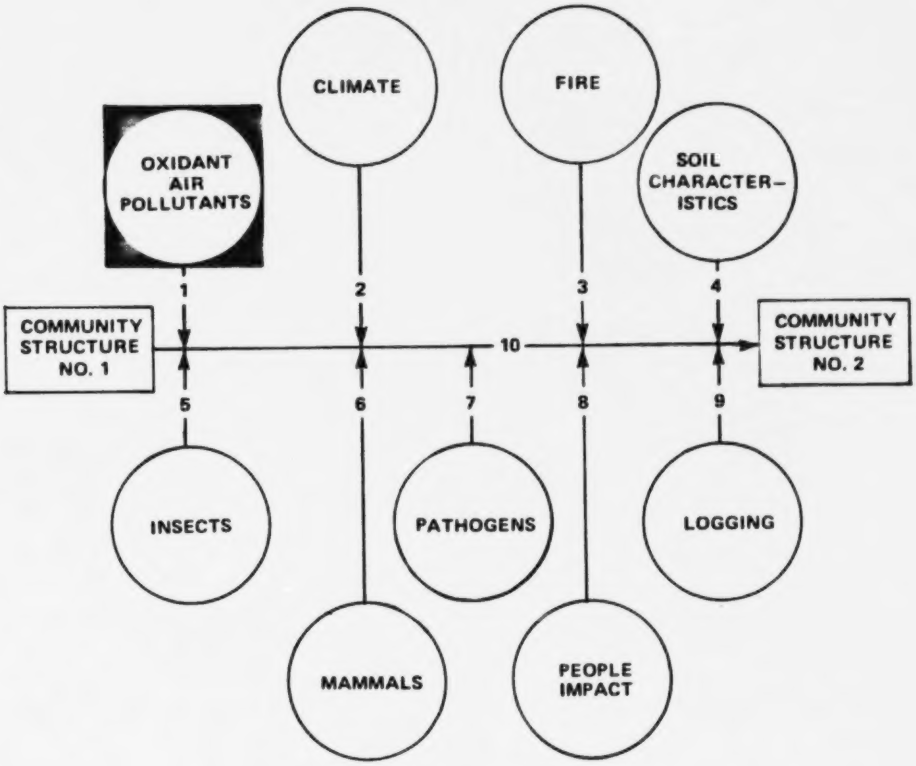


Figure 3-5. Stand-level interactions in a mixed-conifer forest ecosystem (a = direct influence of external factors on trees in stand; b and c = influence of stand condition on nonpathogenic fungi).

A. Effect of plant competition on abundance of cone and seeds
B. Effect of plant competition on characteristics of living trees
C. Effect of plant competition on characteristics of shrubs
D. Effect of plant competition on characteristics of herbs
E. Effect of plant competition on tree mortality

5. Abundance of cones and seeds and predation by cone insects
6a. Abundance of cones and small-mammal predation of cones
6b. Characteristics of forest stands and small-mammal populations
6c. Influence of shrub and herb layer vegetation on small-mammal populations
8a. Smog-caused mortality and morbidity in different tree species with forest stands
8b. Influence of stand conditions on concentration of oxidants
10a. Influence of temperature and evaporative stress on stand structure and composition
12b. Influence of stand condition on temperature and evaporative stress
15a. Influence of bark-beetle caused tree mortality on stand condition
15b. Influence of stand condition on bark beetle population
16a. Influence of soil moisture and temperature on stand characteristics
16b. Influence of stand condition on soil characteristics
19. Influence of stand condition on population dynamics of natural enemies of bark beetles
20. Relationship between smog occurrence and woodpecker population
21a. Influence of pathogen-caused mortality on stand condition
21b. Influence of stand condition on pathogen population
22a. Influence of mycorrhiza fungi
22b. Influence of snags (and downed trees) on nonpathogenic fungi
22c. Influence of stand condition on nonpathogenic fungi

Figure 3-5 (continued). Stand-level interactions in a mixed-conifer forest ecosystem.



1. Oxidant modification of community structure
2. Climate modification of community structure
3. Fire modification of community structure
4. Soil characteristics and their influence on community structure
5. Insect modification of community structure
6. Mammal modification of community structure
7. Pathogen modification of community structure
8. People impact on community structure
9. Logging modification of community structure
10. Predictive capability through integration of submodels for items 1-9

Figure 3-6. Community-succession interactions in a mixed-conifer forest ecosystem.

inventory emphasizes ponderosa and Jeffrey pines, the most dominant species in the climax community, and is stratified according to organizational level: Organism or tree (Figures 3-2 and 3-3), community or stand (Figure 3-4 and 3-5), and, finally, a time-oriented analysis of plant succession in the aggregation of relatively distinct communities or stands that collectively make up the mixed conifer forest ecosystem (Figure 3-6). These figures present in diagrammatic form the complexity of ecosystem interactions at each level of biological organization. Only the interactions considered to be the most important ones guiding the course of plant succession in the several forest plant communities now constituting the mixed conifer forest have been selected by project investigators for immediate investigation. In the case of each interaction, it is important to decide the time frequency at which the selected variables will be measured (i.e., hourly, weekly, or annually). Because this project is the most active effort to date directed toward understanding the effects of ozone and other oxidants on a natural ecosystem, it is dealt with at some length in this chapter.

3.2.3.3 Effects on Primary Producers (Green Plants)--The aim of this section is to evaluate the effects of the chronic exposure of vegetation in natural ecosystems to total oxidants (more than 90 percent ozone) under field conditions or simulated field conditions.

Smith (1974) has suggested three classes of ecosystem response to air pollutants. Those in which vegetation and soils serve only as a sink for pollutants, with no visible vegetation injury; those in which some species, or sensitive individuals within species, are injured and are more susceptible to other stresses; and those in which high dosages cause acute morbidity or mortality of some species. Although these classes are convenient for discussion, they are not clearly separated in space in most situations. More often, these classes of response occur along a gradient of decreasing pollutant exposure, as in the San Bernardino Mountains.

3.2.4 Extent and Intensity of Injury to Overstory Trees in the San Bernardino National Forest

Wert (1969) used aerial photography to determine the extent of oxidant injury to ponderosa and Jeffrey pines in diameter classes larger than 30 cm. Injury was categorized as heavy, moderate, light, or negligible, and it generally decreased with distance from the source area. Of the 64,380 ha (160,950 acres) of ponderosa-Jeffrey type within the forest boundaries, 18,492 ha (46,230 acres) had heavy damage, 21,568 ha (53,920 acres) had moderate damage, and 24,320 ha 960,800 acres) had light or negligible damage. An estimated 1,298,000 trees were affected. Of these, 82 percent were moderately affected, 15 percent were severely affected, and 3 percent had died.

The term "ponderosa-Jeffrey type" is a general term that includes a mosaic of five subtypes described by McBride on the basis of species dominance (National Research Council, 1977). These subtypes are: ponderosa pine forest, ponderosa pine/white fir forest, ponderosa pine/Jeffrey pine forest, Jeffrey pine forest, and Jeffrey pine/white fir forest. The injury by oxidant air pollutants is most intense in the Jeffrey pine types. In the field plots of these various types, as a result of oxidant air pollution, the average area covered by shrubs is only 3.8 percent in the ponderosa types, but 26 percent in the Jeffrey pine types (National Research Council, 1977).

3.2.5 Oxidant Damage to Conifer Species in the 19 Major Study Plots from 1973 to 1974

The first evaluation of oxidant injury to all tree species in the new study plots was completed in September and October 1973. The second evaluation in 1974 offered the first opportunity to compare increases in tree injury and mortality. Tree mortality among ponderosa and Jeffrey pines was about the same in 1973 and 1974. The greatest mortality was in the permanent study plots listed as receiving moderate injury. Possibly the populations in these plots still retain greater numbers of the more susceptible genotypes. In previous years, tree mortality rates for ponderosa or Jeffrey pines in the stands suffering moderate to severe injury were 8 and 10 percent from 1968 to 1972 (Taylor, 1973), 8 percent from 1969 to 1971 (Miller, 1973), and 24 percent from 1966 to 1969 (Cobb and Stark, 1970). The death of weakened trees is usually due to the pine bark beetle (Stark and Cobb, 1968). Mortality has not been observed in tree species other than ponderosa and Jeffrey pine.

Information available from the study of the ponderosa pine subtype suggests that the biomass production of overstory species is diminished in proportion to the oxidant dose received. Parmeter et al. (1962) observed decreases in the height of ponderosa pine that showed injury symptoms. Injured trees did not respond with greater growth during years with more favorable soil moisture content; but uninjured trees (often side by side with injured trees) did increase in height during these years. In another study (National Research Council, 1977) of two populations (one ranging in age from 52 to 71 years and the other from 20 to 39 years) of dominant ponderosa pine stands, the influence of the Los Angeles smog was noted. The width of growth rings before 1940 was compared with those after 1940. After the influence of precipitation on growth was evaluated, a difference of 0.20 cm in average annual growth was attributable to oxidant air pollution injury. A 30-yr-old tree subjected to oxidant air pollution after the influence of precipitation on growth was evaluated would be 24 ft (7.2 m) tall and 7.5 in. (19 cm) in dbh, with one 16 ft (4.8 m) log having a volume of 30 board ft. In comparison, a 30-yr-old tree growing before the injury by oxidant air pollutants (1910-1940) would be 30 ft (m) with a volume of 80 board ft. The impact of oxidant stress on forest growth is apparent.

The growth suppression of ponderosa pine saplings has been demonstrated experimentally by Thompson (1968). Trees grown in a plastic covered greenhouse and provided with charcoal-filtered air (after an initial lag in the growth of shoots and branches in the first years of the experiment) showed dramatically increased growth when compared to trees grown in ambient air outside or trees grown in ambient air outside or trees grown in a greenhouse with unfiltered air. Understory ponderosa pines appeared to be more susceptible to oxidant than larger-size trees (Cobb and Stark, 1970). The incense cedar and sugar pine were the most tolerant to oxidant; however, the sugar pine was present only in very low numbers. The accelerated mortality of ponderosa pines has particular significance in this ecosystem because it is the dominant member of the climax community.

The direct effects of ozone on plant species constituting the shrub layer in the conifer forest are not yet sufficiently understood to permit any conclusions to be drawn. Initial field observations suggest that at least 10 species are obviously injured by total oxidant in areas receiving high dosages. These areas have been subject to exposure for at least 20 years, so some species or subspecies of annual plants may have been completely eliminated.

In a series of experiments, Treshow and Stewart (1973) fumigated native plants growing under natural field conditions. The ozone concentrations required to injure the more prevalent species in the grassland-oak and aspen-conifer communities during 2-hr exposures to 290, 490, 588, and 785 $\mu g/m^3$ (0.15, 0.25, 0.30, and 0.40 ppm) ozone were determined. Seventy common plant species indigenous to the plant communities were fumigated. Of these, 5 species were injured at 290 $\mu g/m^3$ (0.15 ppm), and 20 species at 490 $\mu g/m^3$ (0.25 ppm). These species included grasses, perennial forbs (broadleafed herbs), and trees, and they were distributed over all vegetation zones (see

Table 3-1). The sensitivity of aspen in the aspen-conifer community was considered of great significance. Not only is it dominant, but its presence is vital to integrity of the community. The shade of the aspen is required by the seedlings of the white fir (Abies concolor) and some other species of plants for growth. In the aspen forest of the Wasatch Mountains, where this study was conducted (Treshow and Stewart, 1973), the tree canopy acted as an effective filter. When ozone concentrations of 1770 μg/m^3 (0.9 ppm) were measured in the canopy and in clearings, the concentrations under the canopy were only 196 μg/m^3 (0.1 ppm). It was also noted that though one exposure to 290 μg/m^3 (0.15 ppm) appeared to produce no effect, repeated exposures could injure both growth and reproduction. The implications for possible imbalances in community stability are readily apparent if these plant communities received dosages similar to those typical in the San Bernardino Mountains.

3.2.6 Effects on Reproduction

The effect of ozone injury on herbaceous plant reproduction has been mentioned earlier in this section. Seed production by annuals is influenced mainly by the environmental conditions of the current year, but perennial woody plants, particularly conifers, are erratic seed producers. Factors affecting cone production include age, vigor, seasonal temperature, and soil moisture (Fowells and Schubert, 1951).

Decrease in tree vigor may decrease or totally eliminate cone production or result in a decrease in the size, weight, and germination of the seed produced (Pelz, 1963; Scheffer and Hedgecock, 1955).

Fruit and seeds make up the largest part of the diet of most of the common small mammals on the study sites, particularly the deer mouse (Peromyscus sp.), harvest mouse (Reithrodontomys), chipmunk (Eutamias), ground squirrel (Callospermophilus), and western gray squirrel (Sciurusi griseus

TABLE 3-1 . INJURY THRESHOLDS FOR 2-HOUR EXPOSURES TO OZONE

Species	Injury threshold (ppm ozone for 2 hr)
Grassland-oak community species	
Trees and shrubs	
Acer grandidentatum Nutt	over 40
Acer negundo L	over .25
Artemesia tridentata Nutt	.40
Mahonia repens G Don	over .40
Potentilla fruticosa L	.30
Quercus gambelii Nutt	.25
Toxicodendron radicans (L) Kuntze	over .30
Perennial forbs	
Achillea millefolium L	over .30
Ambrosia psilostachya DC	over .40
Calochortus nuttallii Torr	over .40
Cirsium arvense (L) Scop	.40
Conium maculatum L	over .25
Hedysarum boreale Nutt	.15
Helianthus anuus L	over .30
Medocagp satova L	.25
Rumex crispus L	.25
Urtica gracilis Ait	.30
Vicia americana Muhl	over .40
Grasses	
Bromus brizaeformis Fish & Mey	.30
Bromus tectorum L	.15
Poa pratensis L	.25
Aspen and conifer community species	
Trees and shrubs	
Abies concolor (Gord & Glend) Lindl	.25
Amelanchier alnifolia Nutt	.20
Pachystima myrsinites (Pursh) Raf	over .30
Populus tremuloides Michx	.15
Ribes hudsonianum Richards	.30
Rosa woodsii Lindl	over .30
Sambucus melanocarpa A Gray	over .25
Symphoricarpos vaccinioiders Rydb	.30
Perennial forbs	
Actaeu arguta Nutt	.25
Agastache urticifolia (Benth) Kuntze	.20
Perennial forbs	
Allium acuminatum Hook	.25
Angelica pinnata S Wats	under .25
Aster engelmanni (Eat) A Gray	15
Carex siccata Dewey	.30
Cichorium intybus L	.25
Cirsium arvense (L) Scop	under 40
Epilobium angustifolium L	.30
Epilobium watsoni Barbey	.30
Eriogonum heraclioides Nutt	.30
Fragaria ovalis (Lehm) Rydb	.30
Gentiana amarella L	over 15
Geranium fremontii Torr	under 40
Geranium richardsonii Fisch & Traut	15
Juncus sp	over 25
Lathyrus lanzwertii Kell	over .25
Lathyrus pauciflorus Fern	.25
Mertensia arizonica Greene	.30
Mimulus guttatus DC	over .25
Mimulus moschatus Dougl	under 40
Mitella stenopetala Piper	over .30
Osmorhiza occidentalis Torr	.25
Phacelia heterophylla Pursh	under .25
Polemonium foliosissimum A Gray	.30
Rudbeckia occidentalis Nutt	.30
Saxifraga arguta D Don	under .30
Senecio serra Hook	.15
Taraxacum officinale Wiggers	over .25
Thalictrum fendleri Engelm	over .25
Veronica anagallis-aquatica L	.25
Vicia americana Muhl	over .25
Viola adunca Sm	over .30
Annual forbs	
Chenopodium fremontii Wats	under .25
Callomia linearis Nutt	under .25
Descurainia californica (Gray) O E Schuls	.25
Galium bifolium Wats	over 30
Gayophytum racemosum T & G	.30
Polygonum douglasii Greene	over .25
Grasses	
Agropyron caninum (L) Beauv	over .25
Bromus carinatus Hook & Arn	under .25

anthoni). The gray squirrel is an excellent example of the interactions within this forest and of the potential effects of oxidant air pollution. It is abundant throughout the mixed-conifer-type forest, depending specifically on the pines and oaks for most of its food, cover, and nest sites. This squirrel eats or stores a major portion of the pine and oak seed crops each year. On some yellow pine trees in the study plots, gray squirrels cut more than 2000 cones per tree. During periods of low seed production because of diminished tree vigor, squirrels converge on the few remaining vigorous ponderosa pines and consume about half the seed crop before it matures and reaches the ground. In the areas severely affected by ozone (oxidant), squirrels return to the same trees year after year. After the seed reaches the ground, other small vertebrates, such as mice, seek it out. The habit of preferential seed use by small vertebrates, when considered additively with ozone injury, could seriously reduce the regeneration potential of ponderosa pine.

Thus tree squirrels are a major source of loss of seeds from the ponderosa, Jeffrey, and sugar pines, and of black oak acorns. Vertebrates, then, can have a major effect on the reproduction of these species, particularly because the gray squirrel is only one of numerous species in this forest that feed on conifer seeds and acorns.

Removal of the dominant species in a specific community can have a profound effect on reproduction of other species. Mention has already been made of the effect of the disappearance of the aspens from the aspen-conifer communities. The reproduction of white fir is reduced or eliminated, since the shade required by white fir seedlings is no longer present (Treshow and Stewart, 1973). Other shade-tolerant species are also affected.

Changes in such physical factors as light, temperature (particularly maximums and minimums), relative humidity, and wind speed for forest communities subject to structural alteration by mortality of susceptible species could change the suitability of some sites for growth, reproduction, and reestablishment of survivor species. Some of the possible secondary effects are only speculative until more data are gathered (Miller, 1973).

3.2.7 Effects on Consumer Populations

3.2.7.1 Vertebrate Populations--The effects of oxidant air pollutants on vertebrates can be separated into direct and indirect categories. Direct effects include clinical and pathological alteration of tissues as a result of exposure to ambient air. Indirect effects result from alterations in the numbers or distribution of the plant and animal population exposed to ambient air. For example, if air pollution eliminates or decreases the quantity of a susceptible plant species, the food chain of the consumers that feed on it may break down. The result could be a simpler and less stable ecosystem, with fewer numbers and species of plants and animals.

The clinical and pathological effects of oxidant air pollutants on domesticated vertebrates have been studied in the laboratory. No major references to studies of these effects on free-ranging native species seem to exist. The possible interactions of vertebrates, determined by extrapolation from laboratory studies, are shown in Figures 3-4 through 3-6 for the San Bernardino Mountain ecosystem.

In the San Bernardino Mountains, the aim of the study was to describe the terrestrial vertebrate community within this mixed-conifer forest, particularly in relation to ponderosa and Jeffrey pine stands, and to determine the effects of air pollutants on this community (Figures 3-4 through 3-6).

When changes occur in one part of an ecosystem, the intimate nature of the interrelationships results in changes in many other parts. Any factor that causes change in one component of a system potentially affects all subsystems of that ecosystem. The most important indirect effects of oxidant air pollutants on vertebrates are those resulting in changes in the habitat. Foremost among these effects are those on the vegetation and the successional patterns of the plant community. Because of the high degree of interrelationship and interaction of the vegetation, the fauna, and the inorganic matrix of an ecosystem, effects of air pollution on the vegetation potentially can result in changes throughout the ecosystem. Damage to vegetation is probably the most important effect of chronic, low-concentration air pollution on wildlife. Ponderosa pine, Jeffrey pine, and black oak are all susceptible to injury, and these are the most important trees within the San Bernardino forest as providers of food and habitat for wildlife. A similar selectivity by species doubtless occurs within the shrub and herb layers of the vegetation. The long-term effects will be (1) reduced production of fruits and seeds and (2) elimination of the sensitive plant species and a consequent reduction in the diversity of the vegetation. These effects will in turn lead to a reduction in the abundance and diversity of vertebrate fauna (in the numbers of pine-seed-eating squirrels, for example).

Likewise, Woodwell's (1970) prediction of enhancement of the activity of insect pests and some disease agents (which has been demonstrated in this forest) could lead to an increase in vertebrate species that feed on invertebrates or utilize dead plants for cover. Birds would be the most likely to increase, as would (to a smaller extent) such small mammals as deer mice, which are partially insectivorous.

The indirect effects of ozone through modification of the availability of food for insects, particularly in a conifer forest ecosystem, has received some investigation (Stark and Cobb, 1969; Stark et al., 1968). The weakening of ponderosa pines by chronic exposure to ozone makes them more vulnerable to successful infestation by pine bark beetles (*Dendroctonus brevicomis* and *D. ponderosae*). A positive relationship exists between degree of tree injury and frequency of bark beetle infestation and the relative frequency of bark beetle infestation and the relative frequency of attack by the two species of bark beetles (Stark and Cobb, 1969). The relationship (see Figures 3-3 through 3-6) between tree health and brood productivity and the population dynamics of bark beetles have been a constant threat to pondersoa pines in the San Bernardino Mountains for many years, since before the inception of oxidant air pollution injury (Taylor, 1973). Bark beetles are a key element in accelerating the modification of stand structure.

3.2.7.2 Plant Parasites and Symbionts--Ozone injury to needles of eastern white pine increased infection by *Lophodermium pinastri* and *Aureobasidium pullulans* (Costonis, 1968). These results suggest that leaf tissue of many species may become susceptible to fungi that are normally saprophytes but become parasites when circumstances permit.

Another way that oxidant air pollution could affect this ecosystem is through an alteration in forest moisture. Elimination of vegetation cover allows the exposed soil to dry more rapidly, which would affect soil-burrowing and soil-inhabiting vertebrates. Also, the lower moisture content could reduce or inhibit fruiting-body formation of fleshy fungi. These fleshy fungi are an important food source for tree squirrels and make up a third or more of their diet in some seasons. A reduction in this food source would doubtless result in an even greater utilization of conifer seeds and acorns, thus reducing further the reproductive capacibility of these trees and eventually limiting future food supplies for the squirrel population.

Beneficial mycorrhizal fungi infect the small feeder roots of trees and other plants. The resulting relationship is symbiotic and involves an intimate exchange of minerals and essential metabolites. The host tree benefits through increased efficiency of nutrient uptake from the soil. Any interruption or imbalance of the exchange of materials between the host root tissue and the fungus mantle surrounding it can have deleterious effects on the fungus and the host. Such stresses as air pollution injury to the host undoubtedly disrupt this balance (Hacskaylo, 1973). The feeder rootlet system of ponderosa pines in the San Bernardino Mountains and those of eastern white pine have shown marked deterioration involving a decrease in numbers of mycorrhizal rootlets and their replacement by saprophytic fungi that decay the small rootlets (Parmeter et al., 1962).

Root-infecting fungi such as *Armillaria mellea* and *Formes annosus* are generally more virulent pathogens when they enounter trees already weakened by other stresses. This observation has been made mostly in Europe, where sulfur dioxide was the principal pollutant.

3.2.8 Effects on Decomposers

Although some of the solar energy fixed by producer plants is released by the respiration of these plants and animals, much of it is stored in dead organic matter until released by decomposer organisms at rates that vary greatly with place, season, and kind of organic matter. Generally, one-third or more of the energy and carbon fixed annually in the forests is contributed to the forest floor as litter (mostly leaves) (Ovington, 1957). Because litter is generally related to the quantity of photosynthetic tissue in the ecosystem, it is a useful index of ecosystem productivity.

One of the predicted effects of air pollutants on ecosystems suggested by Woodwell (1970) is a reduction in the standing crop of organic matter, which would lead to a reduction in nutrient elements held within the living system. The evidence discussed earlier definitely shows that primary production is much lower in an ozone-stressed conifer forest ecosystem. This result would be anticipated in all natural ecosystems or agroecosystems under similar stress.

The reservoir of energy and mineral nutrients represented by litter is a very important resource in natural ecosystems with closed nutrient cycles. The growth of new green plant tissue depends on the slow release of nutrients by decomposer organisms. In agroecosystems geared for high production, litter is often removed or burned, and fertilizer is added to the soil; the nutrient cycle is open and subsidized.

In a conifer forest, litter production and decomposition release about 80 percent of the total minerals in the biomass of the stand; the remainder is retained in the living parts of the tree (Millar, 1974). Standing dead material is not considered litter.

In terrestrial ecosystems, most decomposers occupy the mantle of litter on the surface layers of the soil, where they supply the necessary recycling mechanisms to convert dead plant or animal material into humus and eventually into minerals, gases, and water. Small animals, arthropods, fungi, and bacteria exist as a complex in intricate food chains in which they feed on dead material and on one another as well, ultimately releasing the mineral nutrients needed by the producer populations. Without the decomposers, some essential elements (such as calcium, phosphorus, and magnesium) would concentrate in the litter until the supply in the soil was depleted. Growth of green plants would then be seriously limited.

It is not known whether ozone, PAN, or other oxidants could have any direct influence on decomposer organisms other than fungi in the litter layer. But there does appear to be a rapid flux of ozone to soil surfaces. The ozone flux to some kinds of surfaces constituting ecosystems (e.g., vegetation, soil, and water) has been determined by Aldaz (1969), who expressed the flux as molecules/cm^2-sec x 10. The relative fluxes into different surfaces, assuming an ozone concentration of 40 μg/m^3, were: Fresh water, 0.5; snow, 0.9; grass, 1.1; sand or dry grass, 5; and juniper bush, 10. Furthermore, it was found that bare soil destroyed about 75 percent more ozone when dry than when moist. The determination of ozone flux to surfaces may be a far more realistic measure of dose to living organisms than atmospheric concentration of ozone, according to Munn (1970).

In summary, it is anticipated that decreasing litter production by green plants experiencing pollutant stress would result in a similar reduction in the inventory of nutrient elements held within the system, owing to the interruption of nutrient cycling pathways and mechanisms of nutrient conservation (Woodwell, 1970, 1963).

Overall, it can be seen that subtle and simple initial changes may radiate and magnify throughout all trophic levels of the ecosystem. Restoration of the system may be impossible.

3.3 SUMMARY

It should be emphasized that ecosystems are usually subjected to a number of stresses at the same time, not just to a single perturbation (e.g., oxidant).

The effects of oxidants on the San Bernardino Forest graphically demonstrate the changes that occur in natural ecosystems, as discussed earlier. The San Bernardino Forest has been undergoing oxidant stress as a result of long-range transport from Los Angeles, 224 km (140 miles) away, since the early 1940's. Losses of ponderosa and Jeffrey pines, the overstory vegetation, have increased dramatically as pollutant levels have risen. Black oak has also suffered oxidant injury. An alteration in the composition of both plant and animal populations has resulted because of the death of the ponderosa and Jeffry pines.

Oxidant injury to the mixed confier stands of the San Bernardino Mountains beginning in the early 1940's, as indicated above, is well advanced. A similar problem is developing in the forests of the southern Sierra Nevada. Both areas show direct and indirect effects on all subsystems of the forest ecosystem-producers, consumers, and decomposers.

In summary, in the San Bernardino mountains of California:

1. Ozone injury has limited the growth and caused the death of ponderosa and Jeffrey pines. An estimated 1,298,000 trees have been affected. Decrease in cone production has resulted in a decrease in reproduction. Black oak has also suffered injury from ozone.
2. Ozone injury has reduced production of fruits and seeds that make up the diet of most of the common small mammals influences the populations of these organisms.
3. Essential processes, such as recycling of nutrients, may be disrupted, causing a limitation in the growth of vegetation.
4. Death of the predominant vegetation has caused an alteration in the species composition and a change in the wildlife habitat.

The San Bernardino Mountain study illustrates the complexity of the problems caused by environmental pollution. The changes that have occurred in this mountain ecosystem as a result of oxidant transport have already influenced the importance and value of this natural resource to the residents of southern California (Westman, 1977).

The injury to the eastern white pine in the Appalachian Mountains resulting from oxidant transport from the urban northeast has begun a similar sequential change that could degrade this important recreational area. Total oxidant peaks as high as 250 $\mu g/m^3$ (0.11 ppm) were recorded for July 1975. Concentrations exceeding 160 $\mu g/m^3$ (0.08 ppm) were measured in June 1976. These episodes resulted in significant increases in oxidant injury to three categories of eastern white pine in the Blue Ridge Mountains, (Skelly et al., 1977).

Evaluating the contribution of functioning natural ecosystems to human welfare is a complex task and usually involves weighing both economic and social values. However, because natural ecosystems are life support systems, their value should not be quantified in economic terms.

With the passage of time, man has destroyed many of the naturally occurring ecosystems of which he was a part and has replaced them with simplified ecosystems wholly dependent on his care and protection and requiring a large input of energy (Smith, 1974).

Man favors the simple, unstable and synthetic ecosystems, because when they are extensively managed and subsidized by the use of fossil fuels, they are highly productive. An agricultural ecosystem (agroecosystem) is an example of such a simplified ecosystem. The effects of oxidants on agroecosystems have been under study for more than 20 years. The study of effects on natural ecosystems is much more recent.

Plants grown in agroecosystems are largely annuals and can be replaced when they are susceptible to pollutant stress. Natural ecosystems remain in place year after year. Manmade pollutants are undoing relationships developed within these ecosystems over millions of years.

4. EFFECTS OF NITROGEN OXIDES ON TERRESTRIAL ECOSYSTEMS

4.1 EFFECTS OF NITROGEN OXIDES ON AGROECOSYSTEMS

Of the various nitrogen oxides (NO_x) in the ambient air only nitric oxide (NO) and nitrogen dioxide (NO_2) are considered important phytotoxicants. The direct effects of NO_x on vegetation are usually associated with and confined to areas near specific industrial sources. For example, vegetation injury from exposure to NO_2 has been observed near nitric acid factories and arsenals, but there are no published reports on vegetation injury in the field due to NO or other oxides of nitrogen.

The direct effects of NO_x on vegetation are reviewed in this section with emphasis on studies relating NO_x effects to known exposure concentrations and durations. Since most available data pertained to NO_2, this pollutant receives the most attention. Also, when NO_2 was experimentally combined with other pollutants such as SO_2, injury occurred at much lower doses than had been found in earlier studies with NO_2 alone. This suggests that, in certain circumstances NO_2 in conjunction with other gases in the ambient air may behave synergistically.

4.1.1 Factors Affecting Sensitivity of Vegetation to Oxides of Nitrogen

A notable feature of the response of vegetation to NO_2 stress is the varied degrees of NO_2-induced injury. This variation ranges from overt leaf chlorosis and necrosis to alterations of leaf metabolism. These differing responses can be explained by the physiological processes affecting NO_2 uptake into the leaf, pollutant toxicity at target sites and cellular repair capacity. Since plants develop as a consequence of environmental-genotypic interactions, each plant possesses a unique set of structural and functional properties which change continuously in response to genetic and environmental stimuli. These interactions between environmental and genetic factors underlie and explain the dissimilar plant responses to NO_2 exposures.

Information on relative sensitivity (differential response) to NO_2 is summarized in Table 4-1. The three classes - susceptible, intermediate, and tolerant - are approximate because they are based on subjective criteria obtained from several sources. Most of the classifications are developed from experimental fumigations conducted at various locations, at different times of the year, under different environmental conditions using different NO_2 exposure concentrations. Methods for assessing injury, such as percentage of leaves injured, amount of leaf surface affected, defoliation, etc. also varied. Therefore, a plant species considered tolerant by one investigator may be considered susceptible by another. Also, the interaction between genetic and environmental factors that control plant sensitivity is such, that given different sets of environmental parameters or other variables, the relative NO_2 sensitivity of species or cultivars within species can change.

A given plant and its individual leaves, will vary in sensitivity to NO_2, depending on the stage of development. In tobacco (Nicotiana sp.) the oldest leaves became chlorotic, middle age leaves became chlorotic with necrotic lesions, and injury to the younger leaves was limited to necrosis of the leaves of the upper part of the plant (VanHaut and Stratmann, 1967). In Ixora (Ixora coccinea) (MacLean et al., 1968) mustard (Brassica sp.), (Benedict and Breen, 1955) and tobacco (Nicotiana glutinosa) (Benedict and Breen, 1955) the older leaves were more sensitive. In other species such as chickweed (Stellaria media), dandelion (Taraxacum officinale), and pigweed (Amaranthus retroflexus) the middle age leaves were more sensitive. However, in sunflower (Helianthus annuus) middle age and older leaves respond similarly

TABLE 4-1. RELATIVE SENSITIVITY OF SEVERAL PLANT SPECIES TO NITROGEN DIOXIDE (HECK AND TINGEY, 1979; MACLEAN, 1977; TAYLOR AND MACLEAN, 1970; TAYLOR ET AL., 1975; U.S. ENVIRONMENTAL PROTECTION AGENCY, 1971)

Plant Type	Susceptible	Intermediate	Tolerant
Coniferous Trees	*Larix decidua* Mill. (European Larch) *Larix leptolepis* Gord. (Japanese larch)	*Abies alba* Mill. (White Fir) *Abies homolepis* Sieb. & Zucc. (Nikko or Japanese fir) *Abies pectinata* DC (Common Silver Fir) *Chamaecyparis lawsoniana* [Murr.] Parl (Lawson's cypress) *Picea glauca* [Moench] Voss (White Spruce) *Picea pungens glauca*, Regel (Colorado Blue Spruce)	*Pinus mugo* Turra (Knee pine or dwarf mountain pine) *Pinus nigra* Arnold (Austrian pine) *Taxus baccata* L. (English yew)
Field Crops & Grasses	*Avena sativa* L. (Oats) cv. *Clintland 64* cv. 329-80 cv. Pendek *Bromus inermis*, L. (Bromegrass) cv. Sac Smooth *Hordeum distichon* L. (Barley) *Medicago sativa*, L. (Alfalfa) *Nicotiana glutinosa* L. (Tobacco) *Nicotiana tobacum L.* (Tobacco) *Scorzonera hispanica* L. (Viper's grass) *T. incarnatum* L. (Crimson or Italian Clover) *Trifolum pratense* L. (Red clover) *Triticum vulgare*, Vill. (Wheat) cv. *Wells* *Vicia sativa* L. (Spring vetch)	*Gossypium hirsutum*, L. (Cotton) cv. *Acala 4-42* cv. Paymaster *Nicotiana tabcacum*, L. (Tobacco) cv. *White Gold* cv. Bel-B cv. Bel W3 *Poa annua*, L. (Annual bluegrass) *Secale cereale* L. (Rye) *Triticum aestivum* L. (Wheat) *Zea mays* L. (Sweet Corn)	*Nicotiana tabacum*, L. (Tobacco) cv. *Burley 21* *Poa pratensis* L. (Kentucky bluegrass) *Sorghum sp.* (Sorghum) cv. Martin *Zea mays* L. (Corn) cv. Pioneer 509-W cv. Golden Cross
Fruit Trees	*Malus sp.* (Showy apple)	*Citrus sp.* (Orange, grapefruit, tangelo)	*Hosta plantaginea* (Lam.) Aschers (Fragrant plantian lily)

TABLE 4-1 (continued)

Plant Type	Susceptible	Intermediate	Tolerant
	Malus sylvestris Mill. (Apple) Pyrus communis L. (Wild Pear)	Citrus sinensis (L.) Osbeck (Navel Orange)	
Garden Crops	Allium porrum L. (Leek) Apium graveolens L. (Celery) Brassica oleracea botrytis, L. (Broccoli) cv. Calabrese Daucus carota L. (Carrot) Lactuca sativa, L. (Lettuce) Petroselinum hortense Nym. (Parsley) Phaseolus vulgaris, L. (Bean) cv. Pinto Pisum sativum L. (Pea) Raphanus sativus L. (Radish) cv. Cherry Belle Rheum rhaponticum L. (Rhubarb) Sinapis alba (White mustard)	Apium graveolens rapaceum (Celery) Cichorium Endivia, L. (Endive) Ruffee Fragaria chiloensis grandiflora (Pine strawberry) Lycopersicon esculentum, Mill (Tomato) cv. Roma Phaseolus vulgaris humilis Alef. (Bush bean) Solanum tuberosum L. (Potato)	Allium cepa L. (Onion) Asparagus officinalis L. (Asparagus) Brassica caulorapa Pasq. (Kohlrabi) Brassica oleracea acephala DC (Kale) Brassica oleracea capitata L. (Cabbage) Brassica oleracea capitiata rubra L. (Red cabbage) Cucumis sativus, L. (Cucumber) cv. Long Marketeer Phaseolus vulgaris, L. (Bush Bean)
Ornamental Shrubs and Flowers	Antirrhinum majus L. (Giant Snapdragon) Begonia multiflora (Tuberous-rooted begonia) Begonia rex, Putz. (Begonia) cv. Thousand Wonders White Bougainvillea spectabilis Willd. (Bougainvillea) Callistephus chinensis (L.) Nees (China aster) Chrysanthemum sp. (Chrysansanthemum) cv. Oregon Hibiscus rosa-sinensis L. (Chinese hibiscus) Impatiens sultani, Hook. (Sultana) cv. White Imp	Dahlia variabilis Willd. (Dahlia) Fuchsia hybrida Voss (Fuchsia) Gardenia jasminoides Ellis (Cape Jasmine) Gardenia radicans Thunb. (Gardenia) Ixora coccinea L. (Ixora) Ligustrum licidum Ait. (Ligustrum) Petunia X hybrida Hort. Volm.-Andr. (Common Garden Petunia) Pittosporum tobira Ait. (Japanese pittosporum) Rhododendron catawbiense Michx. (Catawaba rhododendron)	Carissa carandas L. (Carissa) Codiaeum variegatum Blume (Croton) Chrysanthemum leucanthemum L. (Daisy) Convallari majalis L. (Lily-of-the-valley) Erica carnea L. (Spring heath) Gladiolus communis L. (Gladiolus) Erica sp. (Heath) Hosta sp. (Plantain lily) Juniperus conferta Parl. (Shore juniper) Rhododendron sp. (Alaska)

TABLE 4-1 (continued)

Plant Type	Susceptible	Intermediate	Tolerant
	Lathyrus odoratus L. (Sweet pea) *Lupinus augustifolius* L. (Lupine) *Nerium oleander* L. (Oleander) *Pyracantha coccinea* Roem. (Fire thorn) *Rhododendron canescens* [Michx.] Sweet (Hoary Azalea) *Rosa sp.* (Rose) *Vinca minor* L. (Periwinkle) cv. Bright Eyes		
Trees & Shrubs	*Betula pendula* Roth. (European white birch) *Melaleuca leucadendra* (L.) L. (Brittlewood)	*Acer platanoides* L. (Norway maple) *Acer palmatum* Thunb. (Japanese maple) *Tilia grandiflora* (Summer) *Tilia cordata* Mill. (Small-leaved European linden)	*Carpinus betulus* L. (European hornbean) *Fagus sylvatica* L. (Beech) *Fagus sylvatica atropurpurea* Kirchn. (Purple-leaved beech) *Gingko biloba* L. (Gingko) *Quercus robur* L. (English oak) *Robinia pseudoacacia* L. (Black locust) *Sambucus nigra* L. (European elder) *Ulmus glabra* Huds. (Scotch elm) *Ulmus montana* With. (Mountain elm)
Weeds	*Brassica* sp. (Mustard) *Helianthus annuus* L. (Common Sunflower)	*Malva parviflora* L. (Cheeseweed) *Stellaria media* [L.] Cyrill (Chickweed) *Taraxacum officinale* Weber (Dandelion)	Amaranthus *retroflexus* L. (Pigweed) *Chenopodium album* L. (Lamb's-quarters) *Chenopodium sp.* (Neetle-leaved goosefoot)

(Benedict and Breen, 1955). In citrus (Citrus sp.) necrosis was most severe on the youngest leaves (MacLean et al., 1968). Emerging or elongating needles of conifers were more susceptible than mature needles (Van Haut and Stratmann, 1967).

Only a few studies have reported the influence of edaphic factors on plant sensitivity to NO_2. Increasing soil moisture increased sensitivity in several weed and vegetable species (Kato et al., 1974a; Benedict and Breen, 1955).

Because of a possible relationship between atmospheric NO_2 and nitrogen metabolism, the influence of soil nitrogen on the plant response to NO_2 has been studied. Rogers et al. (1979) was unable to show differences in NO_2 uptake in corn (Zea mays) or soybean (Glycine max) plants that were grown in soil with varying levels of nitrogen. In contrast, Srivastava et al. (1975c) reported that NO_2 uptake in bean (Phaseolus vulgaris) decreased with increasing levels of soil nitrogen. They also reported that NO_2-induced foliar injury decreased with increasing levels of soil nitrogen. Similar results were found in studies of other vegetables (Kato et al., 1974a, 1974b). Zahn (1975) reported that increasing the available soil nitrogen reduced NO_2-induced foliar injury. However, Troiano and Leone (1974) found that tobacco (Nicotiana glutinosa) grown on a low level of soil nitrogen was more resistant than when grown on a higher level of soil nitrogen. Kato et al. (1974a, 1974b) reported that plants grown on NH_4-N source were more sensitive to NO_2-induced injury and contained higher levels of foliar nitrite after NO_2 exposure than plants grown on a NO_3-N source. Kidney beans (Phaseolus vulgaris) and sunflower (Helianthus annuus) were grown on either ammonium, nitrate, nitrite or minus nitrogen sources. The plants that received either nitrate or nitrite through the nutrient solution contained less nitrite in the foliage following a 3-hour exposure to 7.52 mg/m^3 (4 ppm) NO_2 than plants grown on minus nitrogen or ammonium (Yoneyama et al., 1979). Similarly, tomato (Lycopersicon esculentum) and sunflower (Helianthus annuus) were grown at three levels of nitrogen nutrition ranging from 26 to 260 ppm N (Matsumaru et al., 1979). The plants were exposed to 0.56 mg/m^3 (0.3 ppm) NO_2 for 2 weeks. Plant growth was depressed between 0 and approximately 21% with no clear trend between the nitrogen concentration in the growth media and growth reductions.

Nitrogen nutrition can influence the effects of NO on tomatoes (Anderson and Mansfield, 1979). The plants were grown on either low, medium, or high levels of soil nitrogen and exposed to a concentration ranging from 0 to 0.98 mg/m^3 (0.8 ppm) NO for 50 days. At a low level of soil nitrogen, plant growth increased with increasing levels of NO. At the medium level of soil nitrogen, the 0.49 and 0.98 mg/m^3 (0.4 and 0.8 ppm) levels of NO significantly reduced growth. At the high level of soil nitrogen, all levels of NO reduced plant growth compared to the controls.

Several researchers have studied the effect of light and time of day on plant sensitivity to NO_2. Zahn (1975) noted that alfalfa (Medicago sativa) exposed to NO_2 during the night were injured more extensively than plants exposed during the day. These findings were supported by Czech and Nothdurft (1952) who discovered that the toxic dose for 1-hour exposures of sugar beets (Beta vulgaris) was 10 times greater in the day time, 188 mg/m^3 (100 ppm) than at night, 18.8 mg/m^3 (10 ppm). Van Haut and Stratmann (1967) found leaf injury in oats (Avena sativa) was greater at night, but they also reported that once injury was initiated, the development of necrotic lesions was more rapid on warm sunny days. Kato et al. (1974a, 1974b) determined that vegetable plants were severely injured from NO_2 exposures in the dark and contained higher foliar levels of nitrite than plants exposed in the light. Taylor (1968) reported that bean (Phaseolus vulgaris) plants were injured by 5.6 mg/m^3 (3 ppm) NO_2 in the darkness and that this dose caused as much damage as 11.3 mg/m^3 (6 ppm) NO_2 in the light. Zeevaart (1976) exposed 9 plant species to NO_2 in both light and dark. Eight species exhibited more damage when exposed in the dark. Injury was associated with an increase in nitrite and a decrease in expressed cell sap pH; fumigation of the plants with NH_3 + NO_2 reduced injury. However, with tobacco (Nicotiana glutinosa) light was required for injury to develop and there was no association between injury and either nitrite or cell sap pH. In studies with several vegetable plants, Inden (1975) showed that plants were most sensitive when exposed to NO_2 in the dark. Also leaves treated with the photosynthetic inhibitor DCMU were very sensitive to NO_2 exposures in the light. Plant susceptibility also varies at different times during the day. In a series of 2-hr exposures beginning at 0800-1000 hours and ending at 2000-2200 hours, injury to rye (Secale cereale) plants was greatest at mid-day (Van Haut and Stratmann, 1967).

4.1.2 Mode of Action

Since NO_2-induced perturbations occur at cellular sites within mesophyll tissue, NO_2 uptake into the leaf is required. Absorption is governed by factors regulating gaseous exchange between the atmosphere and the leaf (Nobel, 1974). The NO_2 diffuses from the boundary layer--bulk air interface and terminates with extraction onto mesophyll cell surfaces. The driving force for NO_2 uptake is a concentration gradient and net movement along this gradient is impeded by several leaf resistances: boundary layer, stomatal and mesophyll (residual) resistance.

Rodgers et al. (1979) suggested that NO_2 uptake in corn (Zea mays) and soybean (Glycine max) was directly related to stomatal resistance in the NO_2 concentration range of 0 to 1.09 mg/m^3 (0.58 ppm). Also, NO_2 uptake increased with light intensity through the action of light on stomatal resistance. In studies with beans (Phaseolus vulgaris) and higher NO_2 concentrations over the range of 0 to 13.16 mg/m^3 (7 ppm), NO_2 uptake was controlled more by internal leaf factors (mesophyll resistance) than stomatal resistance (Srivastava et al., 1975a, 1975b); NO_2 uptake was also reported to increase with concentration and decline with increasing exposure time. The NO_2 uptake rate in the dark was approximately one-half the rate in the light. Sunflower (Helianthus annuus) leaves absorbed approximately 14 percent as much NO_2 in the dark as in the light (Yoneyama et al., 1979). Even though NO_2 uptake in the dark is lower, NO_2 exposures in the dark cause greater injury (see 12.2.1).

Nitrogen dioxide reacts in water to produce nitrate, NO_3^-, and nitrite NO_2^- in dilute solutions. Similar reactions would be expected when NO_2 dissolves in the aqueous layer surrounding leaf mesophyll cells. Plants contain the enzymes, nitrate reductase that reduces nitrate to nitrite, and nitrite reductase that reduces nitrite to ammonia which can then be metabolized into organic nitrogen compounds. The nitrate reductase is induced in plants by the presence of its substrate, nitrate. Zeevaart (1974) grew plants with ammonia as the sole nitrogen source and showed that NO_2 exposures induced nitrate reductase activity and enzyme activity increased with NO_2 concentration and duration of exposure. Yoneyama et al. (1979) showed that exposure to 7.52 mg/m^3 (4 ppm) NO_2 for 6 hours increased nitrite reductase activity from 2- to 3-fold.

Faller (1972) grew sunflowers (Helianthus annuus) on a nitrogen free medium and exposed the plants to NO_2 for three weeks at NO_2 concentrations ranging from 0 to 6 mg/m^3 (3.2 ppm). The control plants showed severe signs of nitrogen deficiency and restricted growth. However, the symptoms of nitrogen deficiency decreased and plant growth increased as the NO_2 concentration increased up to 29 percent more than the control levels. Also the nitrogen content of the plants was significantly increased by the exposure. Results of this study show that plants can use atmospheric sources of nitrogen (i.e., NO_2) as their sole nitrogen source. Tomato (Lycopersicon esculentum), sunflower (Helianthus annuus), and corn (Zea mays) derived approximately 16, 22 and 14 percent of their nitrogen, respectively, from NO_2 when the plants were exposed to 0.56 mg/m^3 (0.3 ppm) for 2 weeks (Matsumaru et al., 1979). The absorption rate of NO_2, based on plant dry weight, showed little change with soil nutrition and ranged around approximately 0.8 mg/g dry weight/day for tomato and sunflower to 0.3 mg/g dry weight/ day for corn.

When plants are exposed to high levels of NO_2 the injured leaves frequently exhibit a waxy or water-soaked appearance prior to necrosis. This suggests that cell membranes were disrupted, possibly beyond repair. Berge (1963) suggested that NO_2 may cause cellular plasmolysis implying damage to cellular membranes. He also noted a decline in starch grains.

Kändler and Ullrich (1964) demonstrated that there was a reduced amount of carotene and chlorophyll in leaves after acute NO_2 exposure. Some species of lichens exposed to 3.76 mg/m^3 (2.0 ppm) NO_2 for 6 hours had reduced chlorophyll content; a dose of 7.52 mg/m^3 (4.0 ppm) NO_2 for 6 hours reduced chlorophyll content even further (Nash, 1976). In contrast, Taylor and Eaton (1966) found that chlorophyll content increased following chronic exposures to NO_2. Similarly, Horsman and Wellburn (1975) found that 0.188 to 1.88 mg/m^3 (0.1 to 1.0 ppm) NO_2 applied to pea (Pisum sativum) seedlings increased their chlorophyll content 5 to 10 percent. They also noted the deeper green color and downward curving of the leaves observed by Taylor and Eaton (1966).

In vivo experiments performed by Hill and Bennett (1970) showed that both NO and NO_2 inhibited apparent photosynthesis of oat (Avena sativa) and alfalfa (Medicago sativa) plants at concentrations below those that cause foliar lesions.

The threshold dose for this inhibition was 0.74 mg/m^3 (0.6 ppm) for NO and 1.13 mg/m^3 (0.6 ppm) for NO_2 in 90 minute fumigations, but the inhibition occurred faster for NO than NO_2. The NO_x-induced inhibition of photosynthesis was not permanent. The rate of recovery for a given NO-induced inhibition level was faster than for NO_2. Recovery from NO-inhibited photosynthesis was generally complete within 1 hour. Full recovery from NO_2-induced inhibition of more than 25 percent required more than 4 hours. However, complete recovery of non-foliar injured plants was noted consistently within 1 day following fumigation. In fumigations introducing both NO and NO_2 (1:1) simultaneously, the degree of inhibition of apparent photosynthesis was the same as the sum of that induced by each pollutant when introduced separately.

Capron and Mansfield (1976) found a reduction in the photosynthetic rate of tomato (Lycopersicon esculentum) plants exposed to 0.47 mg/m^3 (0.25 ppm) NO_2, 0.31 mg/m^3 (0.25 ppm) NO or higher concentrations over a 20-hour period. The effect of the two gases in combination was an additive inhibition of photosynthesis. Srivastava et al. (1975a) studied the effects of NO_2 on the gas exchange of the primary leaves of bean (Phaseolus vulgaris). Apparent photosynthesis and dark respiration were both inhibited by NO_2 concentrations between 1.88 and 13.5 mg/m^3 (1 and 7 ppm). The degree of inhibition increased with increasing NO_2 concentration and exposure time. In exposures to NO_2, transpiration rate was effected less than photosynthesis or respiration. Hence, it was proposed that the principal effects of NO_2 on leaf gas exchange occurred in the leaf mesophyll cells and not on the stomata (Srivastava et al., 1975a; Hill and Bennett,1970).

4.1.3 Visible Symptoms of NO_2 Injury

No one visual symptom or set of symptoms reliably indicates plant exposure to NO_2. The diagnosis of injury resulting from NO_2 is often difficult

(Applied Science Associates, Inc., 1976; Taylor and MacLean, 1970). The injury pattern may vary within a species, cultivar, age of leaf, season of year, and/or pollutant dose.

Acute foliar marking produced by high concentrations of nitrogen dioxide exposures are characterized by water-soaked lesions which appear first on the upper leaf surface, followed by rapid tissue collapse. With time these lesions extend through the leaf and produce small, irregular necrotic patches. Necrotic areas are usually white to tan or brown and resemble SO_2-induced symptoms. Lesions occur between the veins of all sensitive plants, and may be located anywhere on a leaf surface, but they are most prominent at the apex along the margins. In monocots, acute NO_2 exposures most often result in yellow to ivory to white necrosis that begins at or just below the tips of the leaf blades. Necrotic margins and striped necrotic lesions between the veins also occur. In most grains and grasses, injury from acute exposures affects the entire width of the leaf blade.

In conifers, acute NO_2 injury usually begins at the needle tips and progresses towards the base. The boundary between healthy and injured tissues is sharply delineated by a brown or red-brown band. Young emerging needles show NO_2 injury at the tips, whereas older needles may develop necrosis in the central or basal portions of the needles. Injured needles may drop prematurely.

Chlorosis is one symptom of chronic NO_2 exposure but is nonspecific and can be a symptom of injury caused by other pollutants. For many chronic exposures, chlorosis precedes the appearance of chronic lesions. Cereal, grains, and corn leaves often develop longitudinal chlorotic bands before necrosis develops. In monocots, chlorosis may occur as transition zones between healthy tissue and the necrotic tips. In some broad leaf plants, chlorosis from chronic NO_2 exposures begins with many small yellow-green areas on the leaf surface which may merge as exposure continues. In some species, chlorosis may be concentrated near the leaf margins.

4.1.4 Dose Response

Exposures to most pollutants, including NO_x, are usually classified arbitrarily as acute or chronic. In experimental fumigations, acute exposures are of short duration at high pollutant concentrations. Chronic exposures are for longer periods (usually intermittent, occasionally continuous) at low concentrations. The ranges of concentrations and durations of exposure (doses) for acute and chronic exposures have not been defined. Most botanic investigators would designate NO_2 exposures of 3 to 5 mg/m^3 (1.6 to 2.66 ppm) or greater for up to 48 hours as acute and those for longer periods at lower concentrations as chronic. However, these definitions do not apply in the field near sources of NO_x emissions. There, an acute exposure is any single exposure causing plant injury. The term "chronic" is applied to a series of exposures that result in injury where no single exposure has an effect by itself.

4.1.4.1 Foliar Injury--Thomas (1952) observed that leaves of plants growing near nitric acid factories often had brown and black spots near the leaf margins. This was an early indication that oxides of nitrogen may be phytotoxic. Haagen-Smit (1951) was one of the first to recognize the importance of NO_2 in causing photochemical smog effects on vegetation. He found that NO_2 added to experimental fumigation mixtures caused plant injury similar to that caused by ozone, but he provided no information on the direct effects on plants. Subsequently, Haagen-Smit et al. (1952) tested NO_2 at 0.75 mg/m^3 (0.4 ppm) on 5 species but observed no injury. Middleton (1958), Middleton et al. (1958) and Thomas (1961) all recognized that NO_2 appeared in photochemically polluted atmospheres as a by-product of combustion, but they postulated that levels were and would continue to be too low to cause vegetation injury.

Korth et al. (1964) found that beans (Phaselous vulgaris), tobacco (Nicotiana tabacum), and petunia (Petunia multiflora) were not injured by 1.88 mg/m^3 (1.0 ppm) NO_2 for 2 hours. Middleton et al. (1958) suggested that 5.64-7.52 mg/m^3 (3-4 ppm) for 8 hours was a threshold concentration that could cause visible injury on pinto bean (Phaseolus vulgaris) leaves.

Heck (1964) fumigated cotton (Gossypium hirsutum), pinto beans (Phaseolus vulgaris) and endive (Cicorium endivia) under controlled conditions with 1.88 mg/m^3 (1.0 ppm) NO_2 for 48 hours and observed slight but definite spotting of leaves. There was no injury produced at 1.88 mg/m^3 (1.0 ppm) NO_2 for 12 hours. In another study, the same species were fumigated with 0.94, 3.76, and 6.58 mg/m^3 (0.5, 2.0, and 3.5 ppm) NO_2 for 21 hours. At exposures of 6.58 mg/m^3 (3.5 ppm) NO_2 mild necrotic spots appeared on cotton (Gossypium hirsutum) and bean (Phaseolus vulgaris) leaves and the endive leaves (Cicorium endivia) were completely necrotic.

Heck and Tingey (1979) conducted a series of short term fumigations which exposed field and vegetable crops to various NO_2 concentrations. In one experiment 10 field and vegetable species were exposed to 15.04, 30.08, or 60.16 mg/m^3 (8, 16, or 32 ppm) NO_2 for 1 hour. At 60.16 mg/m^3 (32 ppm) levels of NO_2, all species showed visual injury. However, at 15.04 mg/m^3 (8 ppm) NO_2 exposure, only brome grass (Bromus inermis) and tomato (Lycopersicon esculentum) exhibited foliar injury. In a second experiment, 22 crop species were given 9 different time and concentration treatments. Exposure duration varied from 0.5 to 7 hours and NO_2 concentrations ranged from 3.76 to 37.6 mg/m^3 (2-20 ppm). An important conclusion from these experiments was that the extent of injury was greatest when the NO_2 levels were high, even for short time periods. For example, cotton exposed to 28.2 mg/m^3 (15 ppm) NO_2 for 1-hour had an injury rate of 27 percent for the three most sensitive leaves. When cotton was exposed to 18.8 mg/m^3 (10 ppm) NO_2 for 2-hours the comparable injury rate was 2 percent. Therefore dose is not always a good predictor of injury, nor is foliar injury a good indicator of the extent to which a plant is injured. A reduction in yield can occur without foliar injury.

4.1.4.2 Growth--Czech and Nothdruft (1952) using 1-hour exposures to 1,880 mg/m^3 (1000 ppm) NO_2 reported that the fresh weight of sugar beet (Beta vulgaris) roots were one-third less than that of the control plants. Zahn (1975) summarized the results of chronic exposures of 10 plant species to 2-4 mg/m^3 (1.06-2.12 ppm) NO_2 for 213 to 1900 hours (Table 4-2). The effects ranged from a 37 percent yield reduction in endive to no effect in roses. Exposures to 1.13 mg/m^3 (0.6 ppm) NO_2 for 30 days reduced the growth of buckwheat (Fagopyrum esculentum) and eggplant (Solanum melongana) (Fujiwara, 1973). The same concentration for 51 days increased the yield of rice (Oryza sativa). Stratmann (personal communication, cited in Taylor et al., (1975) showed that bush bean (Phaseolus vulgaris) growth was slowed by exposure to 1.88 mg/m^3 (1.0 ppm) NO_2 for 14 days. He suggested that a likely threshold dose for injury would be 0.752 mg/m^3 (0.4 ppm) NO_2 over a prolonged time period.

Taylor and Eaton (1966) found reduced fresh and dry weights of unifoliar leaves of pinto bean (Phaseolus vulgaris) plants exposed to NO_2 at 0.62 mg/m^3 (0.33 ppm) for 10 and 19 days. Also, leaves from tomato plants (Lycopersicon esculentum) exposed for 10 and 22 days to 0.21 to 1.17 mg/m^3 (0.11 to 0.62 ppm) were usually significantly smaller than corresponding leaves from non-fumigated plants. One of the most comprehensive reports on the effects of NO_2 on growth and yield is that of Spierings (1971). Continuous exposures of tomato plants (Lycopersicon esculentum) to 0.47 mg/m^3 (0.25 ppm) during the entire growth period (128 days) reduced growth of leaves, petioles and stems. The crop matured slightly earlier and there were substantial decreases in fresh weight yield (22 percent), average fruit weight (12 percent), and the number of fruit

TABLE 4-2. EFFECT OF CHRONIC NO_2 EXPOSURES ON PLANT BROWTH AND YIELD (ZAHN, 1975)

Plant Type	NO_2 Concentration (mg/m^3)	Duration of Exposure (hours)	Effect[a]
Wheat	2	334	No effect on grain yield, but the straw yield was reduced 12%.
Bush Bean	2	639	Yield reduced 27%; Some chlorosis
Endive	2	620	Yield reduced 37%
Carrot	4	357	Yield reduced 30%; Some chlorosis
Radish	4	278	Yield reduced 13%
Currant	2	213	Yield reduced 12%
Roses	4	357	No injury
European Larch	2	537	No injury
Spruce	2-3	1900	7% decrease in linear growth. Growth was decreased 17% in the year following the exposure.

[a] Necrosis did not occur on any plants.

(11 percent). After exposures to 0.94 mg/m^3 (0.5 ppm) for 10 days or 0.47 mg/m^3 (0.25 ppm) for 29 days, fumigated tomato plants were taller than the controls, but stems were smaller in diameter, leaves were not as large, and the fresh weights of the plants were less.

Thompson et al. (1970) exposed navel orange trees to NO_2 continuously for 290 days. When compared to trees exposed to filtered air, those fumigated with NO_2 concentrations ranging from 0.12 to 0.47 mg/m^3 (0.06 and 0.25 ppm) showed a significant increase in fruit drop throughout the exposure period and a significant reduction both in number and weight of fruit at harvest. At Upland, California, ambient and twice ambient levels of NO_2 were added to carbon filtered air supplied to navel oranges (Citrus sinensis) with no effects on leaf drop or yield (Thompson et al., 1971). Recent studies suggested that 0.47 mg/m^3 (0.25 ppm) or less of NO_2 supplied continuously for 8 months will increase leaf drop and reduce the yield of navel oranges (Citrus sinensis) (Taylor et al., 1975).

To determine the effects of NO on the growth of tomatoes (Lycopersicon esculentum), four different tomato cultivars were exposed to 0.49 mg/m^3 (0.4 ppm) NO for 35 days (Anderson and Mansfield, 1979). In two cultivars, total weight, shoot weight and leaf areas were reduced, however, in the other cultivars, NO stimulated plant growth. Exposure of another tomato cultivar to 0.75 mg/m^3 (0.4 ppm) NO for 19 days reduced leaf area, leaf weight and stem weight (Capron and Mansfield, 1977). In the same study, 0.19 mg/m^3 (0.1 ppm) NO_2 had no effect on plant growth and the mixture of 0.19 mg/m^3 (0.1 ppm) NO_2 and 0.49 mg/m^3 (0.4 ppm) NO reduced growth to the same extent as the NO alone (Capron and Mansfield, 1977). Tomatoes grown at three levels of soil nitrogen were exposed to a concentration range of 0 to 0.98 mg/m^3 (0.8 ppm) NO. At harvest (50 days), total weight, shoot weight, and leaf area were measured. At a low level of soil nitrogen, NO stimulated plant growth as reflected in all growth parameters. At a medium level of soil nitrogen, plant growth was decreased at a concentration of 0.49 mg/m^3 (0.4 ppm) NO. At the high level of soil nitrogen, all levels of NO depressed plant growth (Anderson and Mansfield, 1979).

Because of the inter-relationship between concentration and time, there is no single threshold dose for an effect. MacLean (1975) summarized the literature to illustrate the relationship between NO_2 concentration and duration of exposure (dose) for various effects. Three threshold curves are shown in Figure 4-1. These are estimates, as reported in the literature, based on various responses of many plant species, to acute and chronic NO_2 doses. The threshold curve for NO_2 doses that result in the death of plants is short because it is based on limited information. NO_2 doses approaching this threshold result in complete defoliation of some species but are not lethal. The threshold curve for leaf injury is based on observations at many NO_2 doses. The shift in leaf injury from necrosis to chlorosis for NO_2 doses along this curve generally occurred between 10 and 100 hours. Because no measurable effects have been reported for NO_2 doses below the lower curve, it can be considered as the threshold for metabolic and growth effects. NO_2 doses in the area between this curve and the threshold curve for leaf injury are those that do not injure leaves but often result in growth suppression or effects on photosynthesis or other plant processes.

These thresholds (Figure 4-2), assuming that they are reasonable estimates for vegetation in general, can serve as points of reference to evaluate air quality standards for NO_2 in the atmosphere in the absence of other gases and they can be viewed with respect to NO_2 concentrations that occur in the atmosphere.

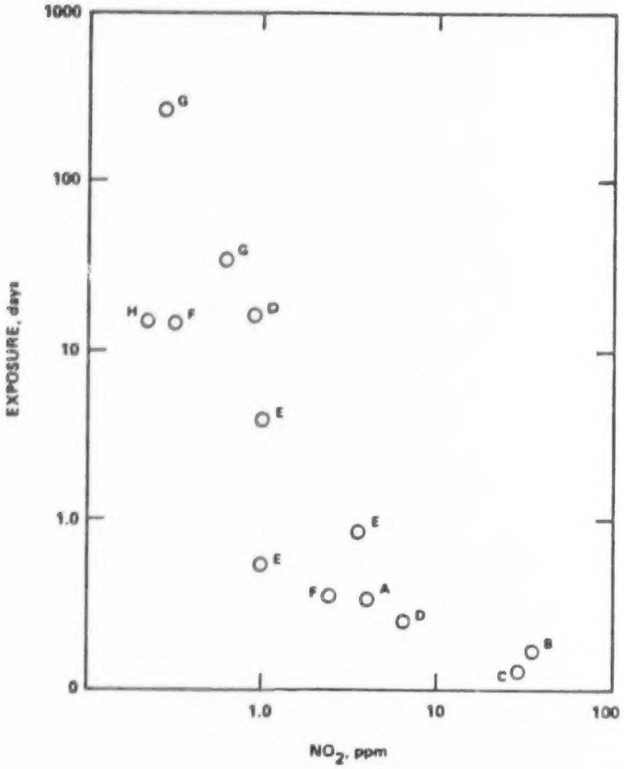


Figure 4-1. Summary of effects of NO$_2$ on vegetation. The points describe a dosage line above which injury was detected.

Source: McLean (1975).

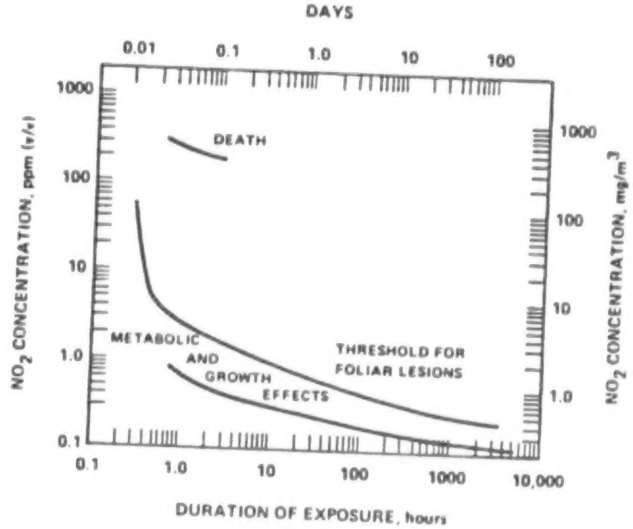


Figure 4-2. Threshold curves for the death of plants, foliar lesions, and metabolic or growth effects as related to the nitrogen dioxide concentration and the duration of exposure.

Source: McLean (1975).

4.1.5. Effects of Gas Mixtures on Plants

Mixtures of dissimilar pollutants often occur in nature. A typical combination includes NO_2 with sulfur dioxide (SO_2) and/or ozone (O_3). Reinert et al. (1975) reviewed information on these types of pollutant combinations. Earlier the assumption was made that NO_x at normal atmospheric concentrations was important only on the basis of its participation in the photochemical oxidant reactions. However, based on studies in which plants were exposed to combinations of pollutants including NO_2 it now appears that ambient concentrations of NO_2 in conjunction with other pollutants may have a direct effect on plants. The results of these studies are described.

4.1.5.1 Nitrogen Dioxide and Sulfur Dioxide--To determine the impact of ambient air pollution on vegetation, NO_2 and SO_2 have been evaluated for their combined effects.

Tingey et al. (1971) found that neither 3.76 mg/m^3 (2.0 ppm) NO_2 nor 1.31 mg/m^3 (0.5 ppm) SO_2 alone caused foliar injury. However, a mixture of 0.188 mg/m^3 (0.10 ppm) NO_2 and 0.262 mg/m^3 (0.10 ppm) SO_2 administered for 4 hours caused foliar injury to pinto bean (Phaseolus vulgaris), radish (Raphanus sativus), soybean (Glycine max), tomato (Lycopersicon esculentum), oat (Avena sativa) and tobacco (Nicotiana tabacum). Exposure to 0.282 mg/m^3 (0.15 ppm) NO_2 in combination with 0.262 mg/m^3 (0.1 ppm) SO_2 for 4-hours caused greater foliar injury. Traces of foliar injury were observed at 0.094 mg/m^3 (0.05 ppm) NO_2 and 0.131 mg/m^3 (0.05 ppm) SO_2.

Matsushima (1971) observed more leaf injury on several plant species from a mixture of NO_2 and SO_2 than that caused by each pollutant alone. He also tested different sequences of exposure. When NO_2 exposure preceded SO_2, the degree of injury was similar to that resulting from individual exposures to either gas. But when SO_2 exposure was followed by NO_2 the degree of leaf injury increased as would be typical of simultaneous exposures to both pollutants. Fujiwara et al. (1973) found greater-than-additive effects when peas (Pisum sativum) were exposed to 0.188 mg/m^3 (0.1 ppm) NO_2 in combination with 0.262 mg/m^3 (0.1 ppm) SO_2. When 0.376 mg/m^3 NO_2 and 0.524 mg/m^3 SO_2 (0.2 ppm of each gas) were used, the effect was only additive.

When a large number of desert species were exposed to either SO_2 or combinations of SO_2 and NO_2 (ratio approximately 4:1) injury from SO_2 and mixtures of SO_2 + NO_2 was similar (Hill et al., 1974). NO_2 decreased the foliar injury threshold of SO_2 on tomatoes (Lycopersicon esculentum), geranium (Pelargonium sp.), and petunia (Petunia sp.) (de Cormis and Luttringer, 1976). Exposure to 0.79 mg/m^3 (0.3 ppm) SO_2 caused no foliar injury but the same concentration of SO_2 in conjunction with 0.94 mg/m^3 (0.5 ppm) NO_2 caused foliar injury. Injury from the gas mixture increased with increasing humidity.

Observations in the vicinity of an arsenal emitting low concentrations of both NO_2 and SO_2 found foliar injury on several conifer species which was attributed to the interaction of the 2 gases (Skelly et al., 1972). The maximum observed 1-hour concentration of NO_x was 0.585 ppm and 2-hour maximum for SO_2 was 0.670 ppm. Effects on growth rate of two tree species were correlated with production activities at the arsenal over a 30 year period suggesting that mixtures of NO_2 and SO_2 may reduce plant growth (Stone and Skelly, 1974).

Bennett et al. (1975) studied the effects of NO_2 and SO_2 mixtures on radish (Raphanus sativus), swiss chard (Beta vulgaris), oats (Avena sativa) and peas (Pisum sativum). Treatments consisted of 1- and 3-hour fumigations with the pollutants separately and with SO_2 and NO_2 (1:1) mixtures in concentrations ranging from 0.33-2.62 mg/m^3 SO_2 (0.12 to 1.0 ppm) and 0.23-1.88 mg/m^3 NO_2

(0.125 to 1.0 ppm). No visible injury occurred on experimental plants treated with NO_2 alone or from exposures to SO_2 concentrations of less than or equal to 1.31 mg/m^3 (0.5 ppm). The minimum exposure doses which caused visible injury to radish leaves were 1-hour exposures to a mixture of 0.94 mg/m^3 NO_2 and 1.31 mg/m^3 SO_2 (0.5 ppm of each gas) or to 1.95 mg/m^3 (0.75 ppm) SO_2 alone. The data indicated that SO_2 and NO_2 in combination may enhance the phytotoxicity of these pollutants, but relatively high doses were required to cause injury.

Reinert et al. (1975) summarized the effects of gas mixtures on foliar injuries to a number of crops (Table 4-3). The data indicate that ambient concentrations of NO_2 and SO_2 may interact to injure vegetation.

A study was conducted to determine the effects of low concentrations of NO_2 and SO_2 singly and in combination on the growth of four grass species (Ashenden, 1979a; Ashenden and Mansfield, 1978; Ashenden and Williams, 1980). Plants were grown and exposed in four small greenhouses which received either charcoal filtered air, 0.21 mg/m^3 (0.11 ppm) NO_2, 0.29 mg/m^3 (0.11 ppm) SO_2 or a mixture of both gases at these same concentrations. The plants were exposed for 103.5 hours per week, which resulted in weekly mean concentrations of 0.13 mg/m^3 (0.068 ppm) NO_2 and 0.18 mg/m^3 (0.068 ppm) SO_2. The plants were harvested monthly and various growth parameters were measured. The results of the experiments are summarized in Table 4-4. Nitrogen dioxide significantly reduced growth parameters of orchard grass and Kentucky bluegrass, but had no effect or a slightly stimulatory effect on the growth of Italian ryegrass and timothy. However, growth parameters of all the species were reduced by SO_2. The combination of NO_2 and SO_2 significantly reduced the growth parameters of all species tested and many of the effects were determined to be synergistic. These data were collected during the winter when the plants were in a period of slow growth which may have increased the pollutant's toxicity. However,

TABLE 4-3. PLANT RESPONSE TO SULFUR DIOXIDE AND NITROGEN DIOXIDE MIXTURES
(TINGEY ET AL., 1971; MATSUSHIMA, 1971; BENNETT ET AL., 1975; HILL ET AL., 1974)

Plant Species	Exposure Chamber[a,c]	SO_2/NO_2 (ppm)	Exposure duration (hours)	Plant Response (% injury)	Mixture Response[b,c]	Plant Age (weeks)
Avena sativa L.	CE	0.75/0.75	1 or 3	0-5	+	4-5
Beta vulgaris var. cicla L.	CE	0.75/0.75	1 or 3	0-5	+	4-5
Lathyrus odoratus L.	CE	0.75/0.75	1 or 3	0-5	+	4-5
Raphanus sativus L.	CE	0.75/0.75	1 or 3	5-8	+	4-5
A. sativa	CE	0.15-0.25/0.1-0.2	4	0	*	2-3
R. sativus	CE	0.15-0.25/0.1-0.2	4	0	*	2-3
Phaseolus vulgaris L.	CE	0.15-0.25/0.1-0.2	4	0	*	2-3
R sativus	CE	0.5/0.5	1 or 3	0-5	+	4-5
Nicotiana tabacum L.	GH	0.1/0.1	4	0-10	+	7-8
Orzopsis hymendoides (R&S) Ricker	F	0.5-0.7/0.15-0.21	2	16	0	*
Populus tremuloides Michx.	F	0.5-0.7/0.15-0.21	2	1	0	*
Sphaeralcea munroana Spach.	F	0.5-0.7/0.15-0.21	2	31	0	*
P. vulgaris	*	1.5/15	1.17	70-75	+	3-4
Lycopersicon esculentum Mill.	*	2.3/13	1	35-85	+	3-5
Cucumis sativus L.	*	2.3/12	0.67	50-100	+	3-4
A. sativa	*	2.4/13	1	40-75	-	3-4
Capsicum frutescens L.	*	2.4/15	1	10-58	+	5-6
P. vulgaris Pinto	GH	0.05-0.25/0.05-0.25	4	0-24	+	3-4
A. sativa	GH	0.05-0.25/0.05-0.25	4	0-27	+	3-4
R. sativus	GH	0.05-0.25/0.05-0.25	4	0-27	+	3-4
Glycine max (L.) Merr.	GH	0.05-0.25/0.05-0.25	4	0-35	+	3-4
N. tabacum	GH	0.05-0.25/0.05-0.25	4	0-18	+	7-8
L. esculentum	GH	0.05-0.25/0.05-0.25	4	0-17	+	5-6

[a] CE, Control environment; GH, greenhouse; F, field.

[b] +, Greater than additive; 0, additive; -, less than additive.

[c] * Not defined.

TABLE 4-4. THE EFFECTS OF NO_2 and SO_2 ALONE AND IN COMBINATION ON THE GROWTH OF SEVERAL GRASSES[1]

Response	Species[2]	Pollutant[3]			Effect Synergistic
		NO_2	SO_2	$NO_2 + SO_2$	
Leaf Area	Orchard grass	21	5	72*	yes
	Kentucky bluegrass	17	28*	84*	yes
	Italian ryegrass	1+	22	43*	yes
	Timothy	30+	11	82*	yes
Number of Tillers	Orchard grass	1	10	32*	yes
	Kentucky bluegrass	9	27*	61*	yes
	Italian ryegrass	17	23*	32*	
	Timothy	6	33*	55*	
Dry Weight green leaves	Orchard grass	7	28*	83*	yes
	Kentucky bluegrass	29*	39*	88*	
	Italian ryegrass	10	28*	65*	yes
	Timothy	14+	25*	84*	yes
Dry Weight dead leaves and stubble	Orchard grass	46*	52*	67*	
	Kentucky bluegrass	27*	37*	57*	
	Italian ryegrass	5	3+	28*	
	Timothy	12	47*	64*	
Dry Weight roots	Orchard grass	11	37*	85*	yes
	Kentucky bluegrass	47*	54*	91*	
	Italian ryegrass	35+	7+	58*	yes
	Timothy	1+	58*	92*	

[1] Data are expressed as percent reductions from the control and are derived from references 127a and 127b. The exposures were for 20 weeks (140 days). Plants were exposed for 103.5 hr/week. The concentrations of NO_2 and SO_2 during exposure were 0.11 ppm which resulted in a weekly average concentration of 0.068 ppm.

[2] The scientific names are: Orchard grass, Dactylis glomerata; Kentucky bludgrass, Poa pratensis; Italian ryegrass, Lolium multiforum; Timothy, Phleum pratense.

[3] Numbers followed by + indicate increase above the control and * indicates significant reductions of the 5% significance level or greater.

the data clearly show that intermittent exposures to ambient concentrations of NO_2 and SO_2 singly and in combination can significantly depress yield parameters of important forage grasses.

Alfalfa (Medicago sativa) exhibited a greater-than-additive response, i.e., a greater inhibition of apparent photosynthesis (CO_2 uptake) when NO_2 and SO_2 were applied together for 2 hours at 0.47 mg/m^3 (0.25 ppm) NO_2 and 0.655 mg/m^3 (0.25 ppm) SO_2 (White et al., 1974). A mixture of 0.282 mg/m^3 (0.15 ppm) NO_2 and 0.393 mg/m^3 (0.15 ppm) SO_2 for 2-hours decreased apparent photosynthesis 7 percent more than when the sum of the two gases was applied independently. At higher concentrations, 0.5 ppm of each gas, the effects were not greater-than-additive. Exposures of alfalfa (Medicago sativa) to 0.62 mg/m^3 (0.33 ppm) NO_2 and 2.62 mg/m^3 (1 ppm) SO_2 at an ambient CO_2 concentration for 1 to 3 hours reduced the photosynthetic rate approximately 50 percent (Hou et al., 1977). When the ambient carbon dioxide concentration was increased to 645 ppm, the inhibitory effect of NO_2 and SO_2 on photosynthesis was less than 50 percent as large as at ambient CO_2 levels. In studies with pea (Pisum sativum) Bull and Mansfield (1974) reported that over the concentration range of 0-0.47 mg/m^3 (0.25 ppm) NO_2 and 0-0.655 mg/m^3 (0.025) SO_2, photosynthesis was inhibited. The duration of exposure was not given. The effect of the two gases was additive in inhibiting of photosynthesis. In bean (Phaseolus vulgaris) when 0.188 mg/m^3 (0.10 ppm) NO_2 and 0.262 mg/m^3 (0.10 ppm) SO_2 were applied individually the pollutants stimulated short-term increases in transpiration, but the combination of NO_2 and SO_2 decreased the transpiration rate (Ashenden, 1979b).

Horsman and Wellburn (1975) studied the effects of NO_2 and SO_2 mixtures on several enzyme systems in peas (Pisum sativum). Peroxidase activity was enhanced somewhat by SO_2 alone but not by NO_2. However, 0.188 mg/m^3 (0.1 ppm)

NO_2 plus 0.524 mg/m^3 (0.2 ppm) SO_2 for 6 days increased the activity by 24 percent. A 100 percent increase occurred when 0.188 mg/m^3 (0.1 ppm) NO_2 plus 5.24 mg/m^3 (2.0 ppm) SO_2 was used for 6 days. The effect was much greater-than-additive. The increase in peroxidase activity was considered a typical stress response of the plant. Similar studies have shown that glutamate dehydrogenase activity is stimulated as a greater-than-additive response by mixtures of NO_2 and SO_2 (Wellburn et al., 1976).

4.1.5.2 Nitrogen Dioxide with Other Pollutants--Matsushima (1971) reported that combinations of NO_2 and O_3 were less injurious to pepper (Capsicum furtesceans) and tomato (Lycopersicon esculentum) than similar concentrations of either gas alone. Loblolly pine and American sycamore (Platanus occidentalis) were exposed to either 0.10 mg/m^3 (0.05 ppm) ozone and/or 0.19 mg/m^3 (0.10 ppm) NO_2 for 6 hours per day for 25 days and effects on injury and growth were determined. At this concentration NO_2 had no deletrious effects on plant growth or injury. The combination of O_3 plus NO_2 yielded the same results as the effects of ozone alone. Reinert and Gray (1977) obtained different results using different pollutant combinations with radish (Raphanus sativus), pepper (Capsicum protescerus) and tomato (Lycopersicon esculentum). They found that NO_2, SO_2 or O_3 were less injurious when used individually than when in combinations of $NO_2 + SO_2$, $NO_2 + O_3$, or $SO_2 + O_3$. De Cormis and Luttringer (1976) found that a mixture of 0.31 mg/m^3 (0.12 ppm) SO_2, 0.56 mg/m^3 NO_2 (0.3 ppm) and 0.2 mg/m^3 (0.1 ppm) O_3 caused extensive leaf necrosis in tomato (Lycopersicon esculentum) within 2 hours.

It is clear from these limited data that levels of NO_2 generally considered below the injury threshold may interact with other common air pollutants to induce vegetation injury. Extensive research is needed to verify this phenomenon under field conditions. It appears that concentrations of NO_2 between 0.188

mg/m^3 (0.1 ppm) to 0.47 mg/m^3 (0.25 ppm) can cause direct effects on vegetation in combination with certain other pollutants.

4.1.6 Summary

Sensitivity of plants to NO_2 varies with species, time of day, light, stage of maturity, type of injury assayed, soil moisture, and nitrogen nutrition.

When exposures to NO_2 alone are considered, the ambient concentrations that produce measurable injury are higher than those that normally occur in the United States. Tomato (Lycopersicon esculentum) plants exposed continuously to 0.47 mg/m^3 (0.25 ppm) for 128 days were reduced in growth and suffered a decreased yield of 12 percent. Leaf drop and reduced yield occurred in naval oranges exposed to 0.47 mg/m^3 (0.25 ppm) continuously for 8 months. Pinto beans (Phaseolus vulgaris), endive (Cicorium endivia), and cotton (Gossypium hirsutum) exhibited slight leaf spotting after 48 hours of exposure to 1.88 mg/m^3 (1.0 ppm). Reduced growth in bush beans (Phaseolus vulgaris) was reported after a 14-day exposure to 1.88 mg/m^3 (1.0 ppm). Other reports cited no injury in beans (Phaseolus vulgaris), tobacco (Nico-tiana tabacum), or petunia (Petunia multiflora) after a 2-hour exposure of the same concentration.

Exceptions to this generality, however, have been observed. For example, the growth of Kentucky bluegrass was significantly reduced (approximately 25 percent) by exposures to 0.21 mg/m^3 (0.11 ppm) NO_2 for 103.5 hours per week for 20 weeks during the winter months. Similar exposures to other grass species generally had no deletrious effect on plant growth.

Nitrogen dioxide concentrations ranging from 0.188 to 1.88 mg/m^3 (0.1 to 1.0 ppm) increased chlorophyll content in pea (Pisum sativum) seedlings from 5 to 10 percent. The significance of the increased chlorophyll is unknown. Some species of lichens, a plant sometimes used as an indicator of the presence of phytotoxic gases, exposed to 3.96 mg/m^3 (2.0 ppm) for 6 hours showed a reduced chlorophyll content.

In contrast to the studies cited on the effects of NO_2 alone, a number of studies on mixtures of NO_2 with SO_2 showed that the NO_2 injury threshold was significantly decreased and that the effects of the two gases in combination were at least additive and usually greater-than-additive. Concentrations at which observable injury occurred were well within the ambient concentrations of NO_2 and SO_2 occurring in some areas of the United States. Neither 3.96 mg/m^3 (2.0 ppm) NO_2 nor 1.31 mg/m^3 (0.5 ppm) SO_2 alone caused foliar injury. Research data from grass species exposed for 20 weeks to concentrations of 0.21 mg/m^3 (0.11 ppm) NO_2 and 0.29 mg/m^3 (0.11 ppm) SO_2 for 103.5 hours per week showed significant reductions in yield parameters ranging from 30 to 90 percent indicating that concentrations of these two gases occurring simultaneously can have major deletrious effects on plant growth.

4.2 EFFECTS OF NITROGEN OXIDES ON NATURAL ECOSYSTEMS

4.2.1 Introduction

Climatic, physicochemical, or biological changes, regardless of their source or nature, will affect the functioning of an ecosystem. Some ecosystems are durable and relatively stable when subjected to a given environmental change; others become unstable given the same change.

It is difficult to assess the complex cause and effect relationships of any pollutant, even when it is studied using only a single organism. When attempting to assess such relationships within populations, communities and ecosystems, the problems become even greater. Additional complications in determining the effects of a single pollutant on natural communities are created by the presence of multiple contaminants that may promote synergistic or antagonistic effects.

The response of ecosystems to environmental changes or perturbations is determined by the response of their constituent organisms. The factors which determine the response of organisms and changes which may occur within ecosystems are discussed below.

Terrestrial, marine, and freshwater ecosystems are functionally important to the integrity of the biosphere. They are important: 1) in the production of food; 2) as global support systems for the recycling of essential nutrients and atmospheric components; 3) in maintaining aesthetically valued natural vegetative communities; and 4) in the assimilation or destruction of many pollutants from the air, water, and soil.

Of the many functions occurring within ecosystems, the flow of energy and nutrients are among the most important. Energy flows through an ecosystem in only one direction while nutrients are recirculated (Whittaker, 1975; Smith, 1974; Odum, 1971; Boughey, 1971).

Nitrogen, one of the nutrients recirculated by ecosystems, is an element essential to all life. It is necessary in the formation of the cells of which all living matter is composed. The production of virtually all food depends directly or indirectly on biologically available nitrogen. The most abundant source of nitrogen is the atmosphere of which molecular nitrogen composes 78 percent (Whittaker, 1975; Smith, 1974). However, most organisms are unable to use molecular nitrogen, therefore, it must be converted into another chemical form. Nitrogen is made available to organisms through the conversion or fixation of molecular nitrogen into biologically available compounds. These transformations of nitrogen are regulated almost entirely by terrestrial and aquatic microorganisms through a complicated series of reactions that are collectively termed the "nitrogen cycle." These transformations are more accurately described as a "nitrogen web" because the image of a simple loop of compounds through which nitrogen successively passes bears little resemblance to reality.

The nitrogen cycle or web has been greatly modified by man, both locally and on a global scale, through agricultural activity, industrial production, fuel burning and waste disposal.

4.2.2 Effects of Nitrates

Ecological effects of increased nitrates can be beneficial or detrimental or both. Effects of both kinds may occur simultaneously, may cause effects in media or in ecological compartments quite removed from those that initially receive the manmade nitrogenous injections. In some natural ecosystems, such as lakes and estuaries, the addition of nitrogen can contribute to eutrophic conditions that are considered undesirable. Nitrate as nitric acid contributes to the acidity of rainfall and some nitrates and related compounds are toxic to plants, animals, and microorganisms.

In most nonagricultural terrestrial ecosystems, the major processes that provide nitrogen for plant growth are mineralization (ammonification and nitrification) of soil organic nitrogen and biological fixation of atmospheric nitrogen. When fluxes of nitrogen enter such systems as a result of human activities, the added inputs in many cases represent a significant fraction of total nitrogen inputs. On the basis of such mass-balance considerations, it seems likely that such fluxes are important nutrient sources that could support increased biotic productivity (National Research Council, 1978).

Except in ecosystems that receive fertilizer or nitrogenous wastes, the most important manmade contributions are likely to be from atmospheric pathways, total (inorganic plus organic) nitrogen loadings in wet and dry precipitation may be equivalent to from 8 to 25 percent of the nitrogen used by plants in different natural ecosystems. Even in heavily managed ecosystems, annual atmospheric fluxes may be substantial; for instance, the calculated total nitrogen contribution from precipitation and from gaseous deposition over the Florida peninsula exceed by a factor of two the amount of nitrogen applied as fertilizer to the agricultural land area within the region (National Research Council, 1978).

Predicting the effects of nitrates and other anthropogenic nitrogen compounds on natural ecosystems involves much greater uncertainties than does prediction of the yield response of an agricultural crop. First, it is far more difficult to determine accurately the actual anthropogenic nitrogen contributions to most ecosystems; this is especially true for terrestrial systems, where the major influxes are from atmospheric deposition. Second, far less is known of the responses of nonagricultural plant communities to increased supplies of fixed nitrogen than is known for cultivated crops. It is possible, however, to estimate the approximate magnitude of anthropogenic nitrogen fluxes to ecosystems, using the limited amount of monitoring data available or mass-balance calculations (see Appendix A of the National Academy of Sciences: Nitrates; an Environmental Assessment) (National Research Council, 1978). Such estimates, and quantitative information about the nitrogen cycle at specific sites in the system under study, make it possible to reach some conclusions about the possible ecological significance of the added nitrogen. In addition, where the data base is more extensive, as it is for a number of lakes in various stages of eutrophication, more quantitative dose-response relationships can be estimated.

Living organisms are exposed to nitrates and related compounds through air, water, soil, and food webs. The rate of exposure depends on proximity to sources and on a great many environmental transport and transformation processes. Biological productivity can be increased deliberately by fertilization, as in agricultural crops, or accidentally through run off to terrestrial or lake systems.

4.2.2.1 Terrestrial Ecosystems--Additions of nitrate and other forms of nitrogen from the atmosphere to ecosystems is an integral function of the terrestrial nitrogen cycle. Higher plants and microorganisms can assimilate the inorganic forms rapidly. The contribution of inorganic nitrogen in wet precipitation (rain plus snow) is usually equivalent to only a few percent of the total nitrogen assimilated annually by plants in terrestrial ecosystems; however total nitrogen contributions, including organic nitrogen, in bulk precipitation (rainfall plus dry fallout) can be significant, especially in unfertilized natural systems.

In absolute terms, atmospheric contributions of nitrate can range from less than 0.1 kg N/ha-yr in the Northwest (e.g., Fredericksen, 1972) to 4.9 kg N/ha-yr in the eastern United States (Henderson and Harris, 1975; Likens et al., 1970). Inorganic nitrogen (ammonia-N plus nitrate-N) loadings in wet precipitation ranged from less than 0.5 kg/ha-yr to more than 3.5 kg/ha-yr in Junge's (1958) study of rainfall over the United States. On the other hand, total nitrogen loads in bulk precipitation range from less than 5 kg/ha-yr in desert regions of the West to more than 30 kg/ha-yr near barnyards and feed lots in the Midwest. Total contributions of nitrogen from the atmosphere commonly range from about 10 to 20 kg N/ha-yr for most of the United States (National Research Council, 1978).

In comparison, rates of annual uptake by plants range from 11 to 125 kg N/ha-yr in selected ecosystems from several bioclimatic zones (National Research Council, 1978). Since the lowest additions are generally associated with desert areas, where rates of uptake by plants are low, and the highest additions usually occur in moist areas where plant uptake is high, the contributions of ammonia and nitrate from rainfall to terrestrial ecosystems are equivalent to about 1 to 10 percent of annual plant uptake. The typical fluxes (additions) of total nitrogen in bulk precipitation, on the other hand, represent from about 8 to 25 percent of the annual plant needs in eastern deciduous and western coniferous forest ecosystems. Although these comparisons suggest that plant growth in terrestrial ecosystems depends to a significant extent on atmospheric loadings, it is not yet possible to estimate the importance of these contributions when compared to biological nitrogen fixation and mineralization of nitrogen in the soil. In nutrient-impoverished ecosystems, such as badly eroded abandoned croplands or soils subjected to prolonged leaching by acid precipitation, nitrogen additions from atmospheric fluxes are certainly important to biological productivity. Such sites, however, are relatively limited in extent. In largely unperturbed forests, recycled nitrogen from the soil organic pool is the chief source of nitrogen for plants, but new nitrogen to support increased production must come either from biological fixation or from atmospheric influxes. It seems possible, therefore, that man-generated contributions could play a significant ecological role in a relatively large portion of the forested areas near industrialized regions.

4.2.3 Effects of Nitrogen Oxides

4.2.3.1 Terrestrial Plant Communities--Studies of plant communities suggest that individual species differ appreciably in their sensitivity to chemical stress, and that such differences are reflected in the changes occurring within plant communities. A common alteration in a community under stress is the elimination of the more sensitive populations and an increasing abundance of species that tolerate or are favored by the stress (Woodwell, 1970). The response of plant populations or species to an environmental perturbation will depend upon life cycles of the plants, microhabitats in which they are growing, and their genetic constitution (genotype). Abundant evidence exists to show that in plant communities undergoing structural changes that reduce environmental or biological variability new species become dominant (Botkin, 1976; Smith, 1974; Miller, 1973; Miller and Yoshiyama, 1973; Woodwell, 1970; Jordan, 1969; McCormick, 1969; Treshow, 1968; Daniel, 1963; McCormick, 1963; Woodwell, 1963; Woodwell, 1962; Keever, 1953). Furthermore, the specific pollutant to which a community is exposed for prolonged periods of time will govern the capacity of the community to recover. In turn, an alteration in the community composition, size of the community, or its rate of energy fixation will influence the animal populations in the vicinity and microorganisms in the underlying soil. These changes, in their turn, will modify the behavioral patterns or alter competition among the prevalent organisms.

Investigations of the influence of nitrogen oxides on economically important plant species have revealed differential susceptibility of plant species, differential effects due to diurnal conditions and age, and difficulties in predicting synergistic effects when a plant population is exposed to more than one pollutant simultaneously. Little information is known about the specific effect of nitrogen oxides on plants in natural communities. Evidence of visible injury to plant communities has seldom been demonstrated. In fact, visible injury may represent only a fraction of the actual harm done to terrestrial communities. Evidence exists, however, that the vigor and survival rate of plants have been affected deleteriously by air pollution (Hepting, 1964). Many instances of injury to higher plants that have been ascribed to pathogens or unknown factors may, in fact, reflect a toxicity associated with nitrogen oxides. Nevertheless, since plants respond simultaneously to many environmental factors, it is frequently difficult to determine which of the potential environmental stresses are responsible for damage to the major species or to the community composition. Thus, it is likely that the response to modest nitrogen oxide stresses would not be recognized because the vigor and visual appearance of plants would be influenced by temperature, soil type and moisture, drainage, interspecific competition, and other factors. Only severe injury could likely be ascribed to a particular pollutional episode (Hepting, 1964).

The agent of stress may have ecological importance inasmuch as the species tolerance to such environmental factors as moisture, temperature, and light, its capacity to compete, and its ability to withstand attack by parasitic organisms, may be affected as well. Moreover, physiological aspects of plant development, including growth, photosynthetic and respiratory rate, and flowering may be influenced by the pollutant. These alterations in the environment and in the plant community will influence energy flow through the ecosystem, its productivity, and the succession of indigenous species.

Studies have been conducted on the effect of air pollutants on ecosystems and plant communities (Parmeter and Cobb, 1972; Wenger et al., 1971). It is the general conclusion of these investigations that further research on the influence of nitrogen oxides on plant communities is required. The available information clearly is too fragmentary to warrant meaningful generalizations at this time.

4.2.3.2 Effects on Animals--Surprisingly little attention has been given to the effect of nitrogen oxides on animal populations or communities. Although laboratory studies of a few individual species have been carried out, it is difficult to extrapolate from these laboratory tests on animals maintained under careful conditions, to populations in the field. The interaction of the various stresses in nature and the uncertainty of cause and effect relationships make any conclusions from laboratory studies quite tenuous. Because species differ enormously in their susceptibility to air pollutants, extrapolation from laboratory tests on one species to potential effects on another is fraught with problems.

One of the few studies conducted on animal populations is that of McArn et al. (1974) who reported that granule-rich microphages appeared in the lung tissues of English sparrows nesting in urban areas with high pollution levels. The microphages were not reported to be present in the lungs of sparrows inhabiting windswept, unpolluted areas. In this study, potential chronic effects could not be determined owing to the relatively short life-span of these birds.

Beyond this limited amount of knowledge, the literature concerning the effects of nitrogen oxides on natural animal populations or communities is extremely sparse. No conclusions can be drawn about whether ambient levels of nitrogen oxides in the atmosphere have an effect on the composition or functioning of animal communities or populations.

4.2.3.3 Effects of Nitrogen Oxides on Microbial Processes in Nature--Microorganisms are essential for the functioning of key processes in terrestrial, marine, and freshwater communities. They are the chief agents for decomposing organic materials in soils and waters. Microfloras are the major agents for destruction of synthetic chemicals introduced into soils and waters. Marine algae are essential for the generation of the oxygen required to sustain life in all higher animals. In soil, the bacteria, fungi, and actinomycetes convert compounds of nitrogen, sulfur, and phosphorus to the inorganic state, thereby providing plants with the required inorganic nutrients. Biologic nitrogen fixation and nitrification are affected solely by these microscopic organisms, which also maintain soil structure and form the humus important to abundant plant growth. In addition, many of the pathogens that are constantly discharged into soils and waterways are eliminated by microbial actions.

In terrestrial and aquatic systems, the major nonbiological processes of the nitrogen cycle involve phase transformations rather than chemical reactions. These transport processes include volatilization of ammonia and other gaseous forms of nitrogen; sedimentation of particulate forms of organic nitrogen; and sorption (e.g., of ammonium ion by clays). Understanding of the biospheric nitrogen cycle and of the factors that control the cycle depends primarily on an understanding of biological principles, especially those of microbial ecology.

The biological transformations involve only six major processes. These processes are discussed here in outline only.

These processes are:

1. Assimilation of inorganic forms of nitrogen (primarily ammonia or nitrates) by plants and microorganisms to form organic nitrogen, e.g., amino acids, proteins, purines, pyrimidines, and nucleic acids. In this report the term ammonia is used for gaseous NH_3 and collectively for NH_4^+ plus NH_3, when there is no need or intention to distinguish between these forms. Ammonium (ion) is used specifically to indicate the cationic form NH_4^+.

2. Heterotrophic conversion of organic nitrogen from one organism (food or prey) to another organism (consumer or predator). Nitrogen is bound in plant or animal protein until the organisms die or as in the case of animals certain products are excreted.

3. Ammonification, the decomposition of organic nitrogen to ammonia. (The ammonia may be assimilated by aquatic or terrestrial plants and microorganisms, may be bound by clay particles in the soil, or it may be converted by

microorganisms to form nitrates in the process termed nitrification. (It may also escape into the air.)

4. Nitrification, the oxidation of ammonium to nitrite and nitrate through microbial action. Nitrates may be assimilated by plants, washed downward through the soil into groundwater or through surface runoff into streams, rivers and oceans or may be transformed into atmospheric nitrogen or reduced to ammonia.

5. Denitrification, implies the gaseous loss of nitrogen, usually as molecular nitrogen (N_2), nitrous oxide (N_2O) or nitric oxide (NO), to the atmosphere as a result of microbial reduction of nitrate. Nitrate is reduced to nitrous oxide (N_2O) and molecular nitrogen (N_2) under anaerobic conditions. Nitrates (NO_3^-) are converted into nitrites (NO_2^-), to nitrous oxide (a gas) (N_2O) and finally into nitrogen gas (N_2) which goes off into the atmosphere. In the soil, nitrites rarely accumulate under acidic conditions but are decomposed spontaneously to nitric oxide (NO), and under alkaline conditions they are biologically converted to N_2O and N_2 (Alexander, 1977a; Brock, 1970). It must be emphasized that this process is anaerobic and that conversion of nitrates to nitrites is extremely sensitive to the presence of atmospheric oxygen. If atmospheric oxygen is present, the conversion does not occur. Some evidence exists for the nonbiological chemical production of nitrogen gas or nitrogen oxides (Delwiche and Bryan, 1976).

6. Biological Nitrogen Fixation is the transformation of atmospheric nitrogen gas into ammonia, nitrates and other nitrogen-containing compounds. The transformation is carried out by a variety of microorganisms. The microorganisms may be either symbiotic (living in the roots of leguminous plants) or nonsymbiotic (living independently in the soil) and the process may be accomplished under aerobic or anaerobic conditions.

The predominant agents of assimilation in water are autotrophic algae and on land, higher plants. In soils, bacteria are important agents of assimilation of inorganic nitrogen. Heterotrophic conversions (e.g., of organic nitrogen in plants to animal protein) are highly complicated processes involving numerous steps, but are not treated in any detail here.

Ammonification and nitrification together constitute the process of mineralization. Bacteria and fungi are the principal agents of ammonification in soils; autolysis of cells and excretion of ammonia by zooplankton and fish are important processes in aquatic systems. Ammonification is important in renewing the limited supply of inorganic nitrogen for further assimilation and growth by plants. Nitrification is mediated primarily by aerobic bacteria that obtain their energy by oxidizing ammonia to nitrite and nitrate. Nitrification converts ammonia, which is volatile but readily absorbable, into nitrate, a nonvolatile but easily leached form.

On an ecosystem scale, denitrification is considered a nitrogen sink since the products (N_2 and N_2O) are readily lost to the atmosphere and most organisms cannot use nitrogen in these gaseous forms. Denitrification is carried out by a ubiquitous group of bacteria that use nitrate as their terminal electron acceptor in the absence of oxygen.

Nitrogen fixation is important as a source of available nitrogen for plant growth in both natural and managed agricultural ecosystems. On a global scale and over millions of years, nitrogen fixation balances the losses by denitrification; on time scales of decades to thousands of years, the two processes may be out of phase without significantly affecting the nitrogen content of the global atmosphere.

Nitrogen fixation is only an indirect source of nitrate in the biosphere, but this process is important in global nitrogen balances, and in the current controversy over the depletion of stratospheric ozone by N_2O.

Numerous texts, monographs, and papers review the nitrogen cycle, (Alexander, 1977a; Delwiche, 1977; Delwiche, 1976; Söderlund and Svensson, 1976; Keeney, 1973; Brezonik, 1972; Brock, 1970; Delwiche, 1970; Bartholomew and Clark, 1965; Hutchinson, 1957; Hutchinson, 1954; Hutchinson, 1944) and other reviews cover specific aspects of the cycle in detail. This discussion emphasizes the processes of the nitrogen cycle that are important to an understanding of the accumulation of nitrate and its transformations in the biosphere. Because the literature dealing with nitrate and the nitrogen cycle is so extensive, no attempt has been made to provide exhaustive documentation here.

As indicated above, of the many functions occurring within ecosystems, the recycling of nutrients is one of the most important. The nitrogen cycle is one example of the cycling of a very important nutrient. Any effect, environmental or biological, which interferes with the cycling process could be detrimental to the lives of plants and animals.

Since microorganisms are critical to the balance of ecosystems, any disturbance in their activities could have serious consequences on a local, regional, or global scale. The potential impact on microorganisms by substances as widespread and pervasive as the nitrogen oxides must therefore be assessed. Surprisingly, this subject has been neglected to date. The few data are based on NO_x concentrations in excess of those found in the atmosphere.

Therefore, the knowledge concerning the potential impact of nitrogen oxides on microbial processes in soils and waters is sparse. Although ambient concentrations probably do not significantly affect biologic processes in natural ecosystems, it is not possible to support this view with experimental data (Alexander, 1977b).

4.3 SUMMARY OF ECOSYSTEM EFFECTS

Ecosystems represent the natural order by which living organisms are bound to each other and to their environment. They are, therefore, essential to the existence of any species on earth, including man, and as life support systems their value cannot be quantified in economic terms.

Ecosystems are important in the production of food, in the regeneration of essential nutrients as well as atmospheric components, in the assimilation or breakdown of many pollutants from the air, water, and soil, and in energy flow. They also give aesthetic pleasure and improve the quality of life.

The nitrogen cycle, an ecosystem function, is essential for all life because nitrogen is necessary in the formation of all living matter. Man has influenced the cycling of nitrogen by injecting fixed nitrogen into the environment or contributing other nitrogenous compounds which perturb the cycle.

Pollutants act as predisposing agents so that disease, insect pests and abiotic forces can more readily injure the individual members of ecosystems. The loss of these individuals results in reduction in diversity and simplification of an ecosystem.

Human activities have unquestionably increased the amounts of nitrates and related compounds in some compartments of the environment. The effects of such increased concentrations of nitrogen compounds may be beneficial or adverse, or both. Effects of both kinds may occur simultaneously, and may be felt in media or in ecological compartments quite removed from those that initially receive anthropogenic nitrogenous inputs.

Assessment of the influence of nitrogen oxides on ecosystems is complicated by several factors. Nitrogen oxides: 1) react with abiotic components of the natural environment as well as with individual organisms; 2) react with varying numbers of dissimilar populations within ecosystems; and 3) may suppress individual populations and thus affect ecosystem functioning.

One function of ecosystems is the cycling of nutrients such as nitrogen. Any effect, environmental or biological, which interferes with the recycling process could have a deleterious effect on the total ecosystem. For example, a reduction in diversity within a plant community results in a reduction in the amount of nutrients present so that growth of remaining individuals decreases.

At the present time there are insufficient data to determine the impact of nitrogen oxides as well as other nitrogen compounds on terrestrial plant, animal or microbial communities. It is possible, however, to estimate the approximate magnitude of anthropogenic nitrogen fluxes to ecosystems, using the limited amount of monitoring data available or mass balance calculations. Such estimates, and quantitative information about the nitrogen cycle at specific sites in the system under study, make it possible to reach some conclusions about the possible ecological significance of the added nitrogen. In addition, where the data base is more extensive, as it is for a number of lakes in various stages of eutrophication, more quantitative dose-response relationships can be estimated.

5. EFFECTS OF SULFUR DIOXIDE ON TERRESTRIAL ECOSYSTEMS

5.1 EFFECTS OF SULFUR DIOXIDE ON AGROECOSYSTEMS

5.1.1 Introduction

The response of plants to SO_2 exposure is a complex process that involves not only the pollutant concentration and duration of exposure but also the genetic composition of the plant and the environmental factors under which exposure occurs. In simplistic overview, this process involves entrance of SO_2 into the plant through leaf openings called stomata, contact within the leaf with wet cellular membranes and subsequent liquid phase reactions resulting in the formation of sulfite and sulfate compounds. The formation of these compounds can initiate changes within the plant metabolic systems that will produce physiological dysfunctions. If sufficient physiological modifications occur, plant homeostasis or equilibrium is disturbed and visible symptoms of injury may or may not be manifested. Plant repair mechanisms can result in a return to homeostasis and recovery; however, should exposure occur again prior to complete recovery, further injury may occur and plant recovery is less probable.

Several plant responses to exposure to SO_2 and related sulfur compounds are possible: (1) fertilizer effects appearing as increased growth and yield, (2) no detectable responses, (3) injury manifested as growth and yield reductions without visible symptom expressions on the foliage or with only very mild foliar symptoms that are difficult to attribute to air pollution without comparing them to a control set of plants grown in pollution-free conditions, (4) injury exhibited as chronic or acute symptoms on foliage with or without associated reductions in growth and yield, and (5) death of plants and plant communities.

In some instances, the addition of low SO_2 concentrations to a plant's environment may induce a fertilizer-like response, but relatively few studies of this phenomenon on agronomic crops have been completed to date; none have shown beneficial effects on natural ecosystems. In view of the scanty data on the subject, only limited consideration of potential beneficial effects of SO_2 exposure can be undertaken at this time, as discussed later.

Plant injury or death may result from continued exposure to high or low pollutant doses. If such is the case, other mitigating factors may also be involved (e.g., abiotic agents or biotic disease-inducing agents such as insects). Depending upon the plant species, exact conditions of the seasonal stage of crop growth, pollutant dose, and environmental conditions, many forms of injury may take place and their relative impact may vary. Symptoms of acute and chronic injury may occur on a given plant simultaneously. Here, injury does not necessarily imply damage (i.e., economic loss). Also, the timing of pollutant exposure in relation to the physiological stage of crop development often determines the relationship of foliar injury to subsequent yield losses.

Before discussing the different types of effects of SO_2 on vegetation, certain background information is provided concerning deposition of SO_2 on plant surfaces, entrance into the plant, and distribution and reaction within the plant after SO_2 entry into plant tissues.

5.1.2 Wet and Dry Deposition of Sulfur Compounds on the Leaf Surfaces

Deposition processes limit the lifetime of sulfur compounds in the atmosphere, control the distance traveled before deposition, and limit the atmospheric pollutant concentrations (Garland, 1978).

There have been several studies of the deposition of particulate material on natural surfaces (Little and Wiffen, 1977; Chamberlain, 1975; Sehmel and Hodgson, 1974). Very large particles are chiefly deposited by sedimentation.

Particles in the range of 1 to 100 μm are also borne towards the surface by turbulence where sedimentation is supplemental to impaction on rough surfaces. Submicrometer-sized particles (e.g., sulfuric acid aerosols) and gases, including SO_2, diffuse by Brownian motion through the thin laminar layers of air close to the plant surface. This may be followed by active uptake by plants. The mean SO_2 deposition velocities are surprisingly similar for a wide range of plant leaf surfaces (Garland, 1978). (Wet deposition of sufur compounds is usually associated with acid rain.)

Dry deposition results in the removal of significant amounts of the larger particles from the atmosphere within 2 or 3 days following emission, but several weeks are required to remove the submicrometer fraction.

5.1.3 Routes and Methods of Entry Into the Plant

Stomata of leaves have been demonstrated to be the major avenues of SO_2 entrance into plants. Although this is a widely accepted conclusion that has been presented in numerous reviews (Guderian, 1977; U.S. EPA, 1973; Thomas and Hendricks, 1956; Katz, 1949), there is still controversy as to the importance of stomatal movement relative to plant biochemistry in determining plant sensitivity. Many factors that govern the mechanism of stomatal opening and closing have been determined to be independent of SO_2 concentrations to which a plant is exposed. Physical factors such as light, leaf surface moisture, relative humidity, and soil moisture availability influence stomatal opening and closing and play a major role in plant sensitivity by limiting passive entry of SO_2 into the leaf (McLaughlin and Taylor, 1981; Domes, 1971; Spedding, 1969; Meidner and Mansfield, 1968; Setterstrom and Zimmerman, 1939). These factors must therefore be considered when determining plant sensitivity or tolerance to entry of SO_2.

The rate of absorption of SO_2 by plants varies not only among species, but is also influenced by previous exposures to SO_2. Rates of SO_2 absorption and of translocation of absorbed sulfur were determined in sugar maple (Acer saccharum Marsh.), big toothed aspen (Populus grandidentata Michx), white ash (Fraxinus americana L.) and yellow birch seedlings (Betula lutea Michx. f.). Bigtooth aspen, a species sensitive to SO_2, had the highest absorption rate with no prefumigation and sugar maple, a tolerant species, had the lowest. The rate of sulfur absorption was reduced in all species except white ash, a species of intermediate sensitivity, after prefumigation with SO_2 at 1970 $\mu g/m^3$ (0.75 ppm) for 20 to 36 hrs. (Jensen and Kozlowski, 1975). The relationship between species sensitivity and absorption rate thus changed with the prefumigation treatment. The sulfur content of foliage in all species increased with SO_2 fumigation. Eight days after fumigation with $^{35}SO_2$, varying amounts of the labelled sulfur were translocated throughout the plants, including roots (Jensen and Kozlowski, 1975). Subsequent effects were not indicated.

Sulfur dioxide has been shown both to increase and decrease stomatal resistance and thus affect potential photosynthetic performance (Hallgren, 1978). Sulfur dioxide induced the closure of "Pelargonium x hortorum" stomata, especially when they had been fully opened, and necrosis was not averted (Bonte et al., 1975). Kodata and Inoue (1972) demonstrated that SO_2 entered leaves of Pinus resinosa (Redpine) through stomata and accumulated in the cells around stomata for some time before diffusing inward through the leaf; i.e., internal diffusion was slower than diffusion into the leaves.

Once SO_2 has entered a leaf, it may induce stomata to remain open for longer periods of time or to open wider than before fumigation. However, exposure of plants to SO_2 (1360 $\mu g/m^3$, 0.5 ppm) at relative humidities above 40 percent caused an increase in stomatal opening (Majernik and Mansfield, 1970;

Mansfield and Majernik, 1970). A 3-minute fumigation with 6550 μg/m^3 (2.5 ppm) SO_2 increased carbon dioxide uptake and stomatal opening in white mustard, Brassica hirta Inoench (Sinapsis alba B + B) plants. However, suppressed carbon dioxide uptake and stomatal closure have also been noted when the same concentration. (Buron and Cornic, 1973).

5.1.4 Cellular and Biochemical Changes

Based on the available literature, it is difficult to associate SO_2-induced biochemical and/or physiological changes at the cellular level with subsequent effects on photosynthetic activity or growth and yield. Numerous studies have utilized detached leaves and/or isolated chloroplasts in culture solutions for evaluation of biochemical or physiological effects, but their use for field estimations under ambient conditions remains limited.

Recent studies have also shown the occurrence of a variety of SO_2-induced biochemical effects such as: enzyme inhibition (Pahlich, 1973; Ziegler, 1972; Pahlich 1971); interference with respiration (Haisman, 1974); interference with energy transduction (Ballentyne, 1973); interference with lipid biosynthesis (Malhotra and Kahn, 1978); alterations in amino acid content and quality (Godzik and Linskens, 1974); and chlorophyll loss (Rao and LeBlanc, 1965). Pahlich (1975) has rationalized some of this diverse list of effects in terms of sulfite and sulfate accumulation by exposed plant tissues.

Vogl et al. (1965) attempted to integrate biochemical responses with the type and magnitude of resultant plant effects (Table 5-1). In Table 5-1 degrees of injury are classified from A to E, i.e., from no visible injury to "catastrophic" in Vogls' terminology. Development of models is necessary if changes in physiology (biochemical responses) of specific plant species are to be related to altered growth and productivity, both qualitatively and quantitatively. The relationship between biochemical changes or responses and visible injury at various SO_2 exposure levels remains to be better defined.

TABLE 5-1. RELATIONSHIP OF BIOCHEMICAL RESPONSE TO VISUAL SYMPTOMS OF PLANT INJURY

Degree of Injury	Description of Injury					
	Visible symptoms	Symptoms of biochemical injury in leaf cells	Injury To:		Ability to recover in:	
			Assimilation organs	Whole plant	Assimilation organs	Whole plant
A	none	stress on buffer systems	none	none		
B	not detectable	photosynthesis adversely affected, diminished assimilation rate	temporary impedance of gaseous exchange	not detectable	very quick, completely	
C	loss of assimilation capacity through:	diminished activity of enzymes	prolonged impedance of gaseous exchange	reduced growth (deficiency (conditions)	slowly, completely	slowly, completely for perennials
	1) premature death of assimilation organs (leaves, needles)	effect upon chlorophyll				
	2) diminished growth of new tissues (shorter needles, etc.)					
D	necrosis of the assimilating and active plant tissues	death of cells through protein and enzyme degradation	irreversible injury: necrosis of some assimilation organs or parts thereof	loss of assimilation capability	quick, not completely, sometimes (for isolated tissues) not any more	slowly completely for perennials
E	destruction of all important assimilatory plant tissues	death of organs	irreversible injury to all assimilation organs	destruction of assimilation capability	none	sometimes (for isolated tissues)

Vogl, et al., 1965.

With SO_2, which upon absorption is further oxidized to $SO_3^=$ and $SO_4^=$ and subsequently incorporated into S-containing amino acids and proteins, the rate of entry is particularly important to determining toxicity. Plants have an inherent, and apparently species-dependent, capacity to absorb, detoxify, and metabolically incorporate SO_2 and may absorb low concentrations of SO_2 over long time periods without damage. Thomas et al. (1943), for example, exposed alfalfa to SO_2 continuously at 520 $\mu g/m^3$ (0.20 ppm) for 8 weeks without adverse effects. Toxicity to SO_2 may occur during short episodes when the SO_2 to $SO_4^=$ conversion capacity rate is exceeded and the extremely toxic sulfite ($SO_3^=$) form, a partially oxidized metabolic intermediate, accumulates (Ziegler, 1975). During longer exposures at lower SO_2 concentrations, SO_4 may accumulate as the capacity for metabolic incorporation of $SO_4^=$ is exceeded, and chronic symptoms may appear. It is therefore reasonable to expect that either no effects or beneficial effects may be associated with low-level SO_2 exposures; but detrimental (even fatal) toxic effects may occur at increasingly higher SO_2 exposure levels once metabolic capacities are exceeded for conversion of SO_2 to $SO_3^=$, $SO_3^=$ to $SO_4^=$ and the transformation of $SO_4^=$ in the leaf.

5.1.5 Beneficial "Fertilizer" Effects

Under certain conditions, atmospheric SO_2 can have beneficial effects on agronomic vegetation (Noggle and Jones, 1979). Sulfur is one of the elements required for plant growth and Coleman (1966) reported that crop deficiencies of sulfur have been occurring with increasing frequency throughout the world. The sulfur required to maintain high crop production range from 10 to 40 kg/ha per year. Figure 5-1 presents a map of sulfur deficient soils of the United States (The Sulphur Institute, 1979).

Cowling et al. (1973) found beneficial effects of SO_2, such as increases in yield and sulfur content, in perennial ryegrass that was grown with an

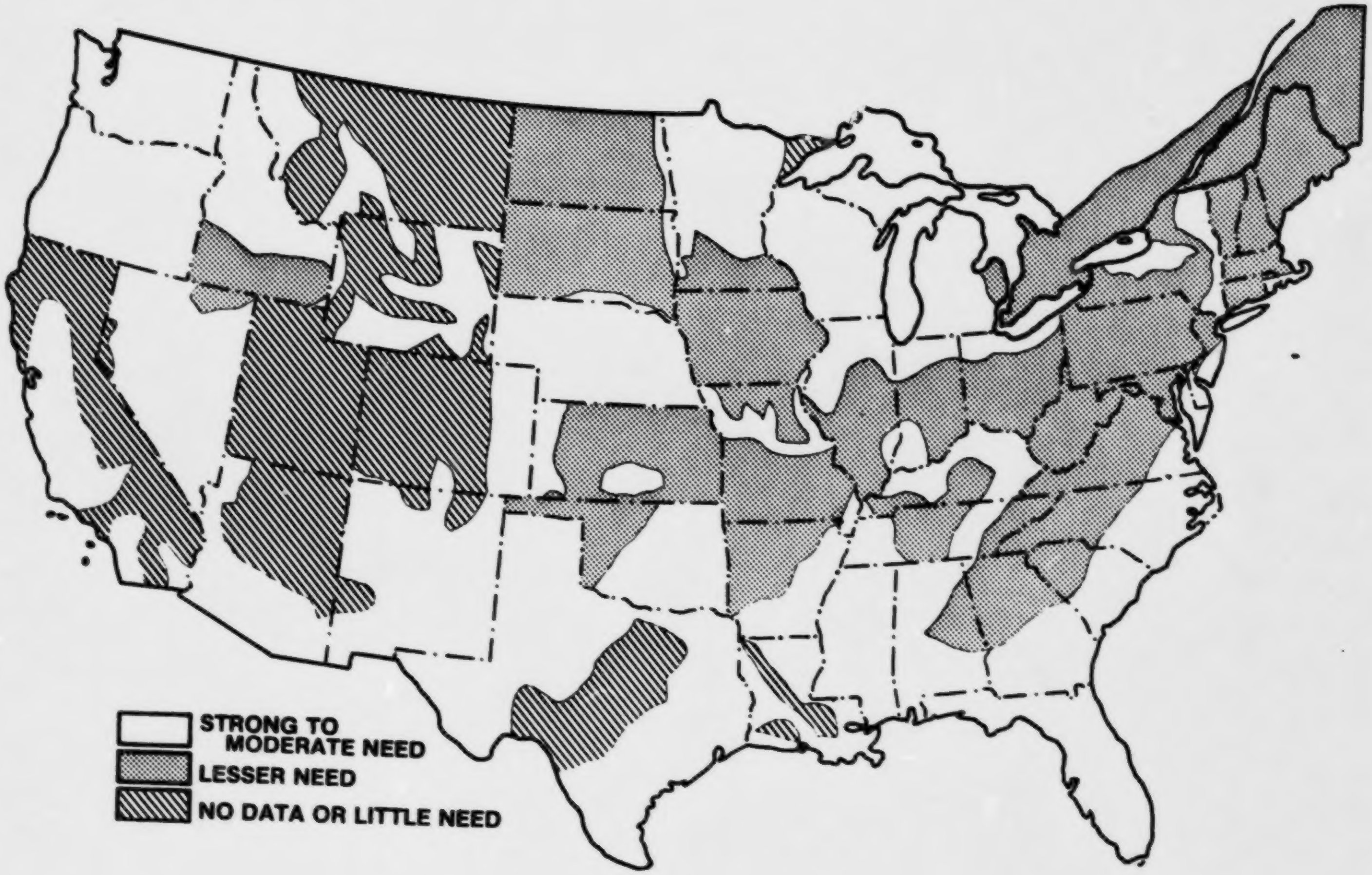


Figure 5-1. **Map of the United States indicating major areas of sulfur-deficient soils.**

Source: The Sulfur Institute (1979).

inadequate supply of sulfur to the roots. Faller (1970) conducted a series of experiments to determine effects of varying atmospheric concentrations of SO_2 on sunflower, corn, and tobacco. In these studies, plants were grown in nutrient media containing adequate supplies of all essential elements except sulfur, which was low. Plants grown in the atmosphere without SO_2 developed sulfur-deficiency symptoms within a few days. In other treatments, total plant yield increased to some extent when increasing concentrations of SO_2 were added to the atmosphere during plant growth. For tobacco, the total dry weight increased by up to 40 percent. Yields of leaves and stems alone increased by 80 percent while dry weights of tobacco increased even at the highest SO_2 concentration used (1490 $\mu g/m^3$, 0.57 ppm); sunflower and corn had their highest biomass at SO_2 concentrations of 1050 $\mu g/m^3$ (0.40 ppm) and 520 $\mu g/m^3$ (0.20 ppm), respectively. Beyond these concentrations, visible injury was observed. Additional studies by Faller (1970) with ^{35}S suggest that up to 90 percent of a plant's sulfur requirements may originate from the atmosphere under the specific experimental conditions.

No monitoring or handling procedures for SO_2 exposures were presented in a study by Thomas et al. (1943); however, its results indicated that SO_2 could serve as a source of nutrient S when alfalfa, grown in sulfur deficient solutions, was fumigated with approximately 260 $\mu g/m^3$ (0.10 ppm) SO_2 for 6 to 7 hr/day, 6 days/week for the growing season, but had little effect when the growth medium contained sufficient sulfur.

Noggle and Jones (1979) reported the results of a 2-year study comparing the contributions of soil and atmospheric sulfur to the sulfur requirements of cotton and fescue when the plants were potted in soil and ^{35}S was added as the S nutrient. Cotton was more efficient than fescue in accumulating sulfur from the atmosphere. The amount of sulfur accumulated from the atmosphere was apparently influenced by the amount of sulfur supply in the soil relative to the sulfur requirements of the plant. A crop grown in a sulfur-deficient soil will accumulate more sulfur from the atmosphere than the same crop grown in a soil that has an adequate supply of sulfur. Noggle and Jones (1979) also showed that cotton grown in specifically designed growth containers in the vicinity of certain coal-fired power plants accumulated significant amounts of atmospheric sulfur (as SO_2) and produced significantly more biomass than those grown at a location farther from the industrial source of sulfur. Thus, under appropriate conditions, such as with sulfur-deficient soils, the atmosphere can be an important source of sulfur for plant requirements. It should be noted, however, SO_2 monitoring data were not presented in the report.

Similar stimulatory responses of Oryzopsis hymenoides (a desert grass) were noted following continuous exposure to SO_2 concentrations of 80 $\mu g/m^3$ (0.03) and 160 $\mu g/m^3$ (0.06 ppm) for 6 weeks (Ferenbaugh, 1978). The noted increases in productivity expressed as mg dry wt/plant were not statistically different from the control plants, but the trends were stable for these doses. Exposure to 340 $\mu g/m^3$ (0.13) and 660 $\mu g/m^3$ (0.25 ppm) SO_2 under identical conditions however, resulted in foliar symptoms and decreased productivity.

Studies that have demonstrated beneficial effects, as well as those demonstrating detrimental effects, must be evaluated in terms of their single influence on one crop. There is little doubt that direct application of sulfur as a nutrient to certain crops grown under borderline or sulfur-deficient conditions may result in increased productivity for that crop. Plants normally take up sulfur in the form of sulfate via the roots; however, they can also utilize SO_2 taken up through the leaf stomata. Faller (1971) has shown that tobacco plants can utilize SO_2 as a sulfur source in deficient soils. Studies of this type (Faller, 1970) have led some individuals to conclude that SO_2 emitted from industrial sources is actually beneficial as an aerial fertilizer for plants growing in sulfur deficient soils (Noggle and Jones, 1979; Terman, 1978). The situation is not as simple as portrayed. A small amount of atmospheric SO_2 can be nutritionally beneficial to plants in the short term. In the long term, however, large, uncontrolled, and frequent applications of sulfur, such as SO_2, can be detrimental. Not all plant species have the same nutritional requirements. In addition, the rate at which plant species assimilate sulfur is influenced by such variables as the physiological status of the plants, age and time during the growing season when the application occurs, availability of soil nutrients, and light intensity. When more sulfur is available than can be assimilated by plants, it is accumulated in the leaf tissue (Cowling and Koziol, 1978; Thompson and Katz, 1978; Legge et al., 1976; Ulrich et al., 1967). Sulfur accumulation in the leaf can reach toxic levels and adversely affect plant growth (Linzon et al., 1979; Katz, 1949). Growth rates of leaf tissues, available nutrient supplies, and environmental factors affecting stomatal opening and closing should all be considered as influencing the rate of sulfur accumulation in plant tissues (Bell and Clough, 1973).

The effects of nutrient forms of nitrogen being delivered to the plant along with SO_2 in plumes under field conditions has not been investigated. However, Cowling and Lockyer (1976) demonstrated that ryegrass (the S 23 cultivar), when grown under sulfur (S) deficiency and at low nitrogen (N), did not respond to 50 $\mu g/m^3$ (0.02 ppm) SO_2 for 85 days whereas plants grown at high N under the same exposure conditions responded with a 227 percent yield increase and S-deficiency symptoms were alleviated. Data presented by Cowling and Jones (1971) previously showed that at high levels of N and inadequate levels of S, nitrate-nitrogen accumulated in ryegrass, thus indicating that protein synthesis was inhibited. Long-term natural ecosystem studies showing the beneficial effects of SO_2 deposition are not available, whereas those showing detrimental effects are (Legge et al., 1981; Legge, 1980; Winner et al., 1978; Winner and Bewley, 1978a). Since agronomic and natural ecosystems are often physically proximal to one another, further research on the potential influence of sulfur compounds to each singly and collectively is greatly warranted.

The Sulphur Institute (1971) has published a review of crop response to sulfur and the reader is referred to that review for more information on beneficial effects of sulfur on plants.

5.1.6 Acute Foliar Injury

This type of injury occurs following rapid absorption of a toxic dose of SO_2 and results at first in marginal and intervenal areas having a dark green, watersoaked appearance. After desiccation and bleaching of tissues, affected areas become light ivory to white in most broadleaf plants. Some species show darker colors (brown or red), but an exact line of demarcation characteristically exists between symptomatic and asymptomatic portions of leaf tissues. Bifacial necrosis is common. In monocotyledons (corn, grasses), foliar injury occurs at the tips and in lengthwise strips along parallel veins (U.S. EPA, 1976).

In conifers, acute injury on foliage usually appears as a bright orange red tip necrosis on current-year needles, often with a sharp line of demarcation between the injured tips and the normally green bases. Occasionally, injury may occur as bands at the tip, middle, or base of the needles (Linzon, 1972). Recently incurred injury is light colored; but later, bright orange or red colors are typical for the banded areas and tips. As needle tips die, they become brittle and break, or whole needles drop from the tree. Pine needles are most sensitive to SO_2 during the period of rapid needle elongation, but injury may also occur on mature needles (Davis, 1972a).

5.1.7 Chronic Foliar Injury

Visible plant injury not involving collapse and necrosis of tissues is termed chronic injury. This type of visible injury is usually the result of variable fumigations consisting of either short-term, high-concentration or long-term, low-concentration exposures to SO_2. It has also been referred to as "sulfate injury" since a slow accumulation of sulfate is an end result of such exposures (Daines, 1968). Within substomatal cavities, SO_2 reacts quickly with intercellular water to form sulfite and bisulfite. These substances are slowly oxidized to sulfate which is approximately one-thirtieth as toxic as sulfite and bisulfite (Thomas, 1951). If the capacity of plant tissues to convert sulfite and bisulfite to sulfate is not exceeded or sulfate elimination processes are not overwhelmed, visible expression of symptoms will not occur. However, as sulfite and bisulfite ions are formed and as sulfate accumulates to phytotoxic levels, then chronic symptoms first appear as various forms of chlorotic (yellowing) patterns. As sulfite and bisulfite ions continue to accumulate, destruction of individual chloroplast membranes or reduction of chlorophyll production ensues, resulting in reddening or bleaching of cells without necrosis (Thomas, 1951). Following such accumulations, there is a fine distinction between chronic and acute symptom expressions. Sulfate levels in plants ambiently exposed to SO_2 have been demonstrated to be several times greater than those in control plants (Linzon, 1958).

In broadleaf plants chronic injury is often expressed in the tissues located between the veins, with various forms of chlorosis predominating. Chlorotic spots or mottle may persist following exposure or may subside and disappear after pollutant removal or other changes in environmental conditions (Jacobson and Hill, 1970). Chronic effects of SO_2 in conifers are generally first expressed on older needles (Linzon, 1966). Chlorosis of tissues starting at the tips progresses down the needle towards the base, i.e., symptoms progress from the oldest to youngest tissues. Advanced symptoms may follow, involving reddening of affected tissues (Linzon, 1978).

5.1.8 Foliar Versus Whole Plant Responses

The presence of acute or chronic foliar injury is not necessarily associated with growth or yield effects. Furthermore, when present, the degree of foliar injury may not always be a reliable indicator of subsequent growth or yield effects.

Yield effects in the absence of foliar injury, for example, have recently been reported for soybean in field fumigation experiments (Sprugel et al., 1980; Heagle et al. 1974) and in chamber exposures (Reinert and Weber, 1980). Sprugel et al. (1980), utilizing the Zonal Air Pollution System (ZAPS), reported significant yield reductions in Wells soybeans exposed to mean SO_2 concentrations of 240, 260, 500, 660 or 940 $\mu g/m^3$ (0.09, 0.10, 0.19, 0.25, or 0.36 ppm) for an average of 4.2 hr/day intermittantly for 18 days during July and August 1978, but visible leaf injury was seen only at the highest SO_2 concentration. It must be noted that characteristics of the ZAPS permits significant variation in pollutant concentrations. For example, in 1977, within experiments reporting a mean SO_2 concentration of 790 $\mu g/m^3$ (0.30 ppm), the actual concentration ranged from 0.00 to 3140 $\mu g/m^3$ (0.00 to 1.20 ppm) SO_2 (Miller et al., 1980). The "ZAPS" type of exposure system, however, tends to simulate ambient conditions near a point source.

Reinert and Weber (1980), in a greenhouse chamber study of O_3 + SO_2 interaction, exposed Dare soybeans 4 hr/day, 3 times per week, for 11 weeks. They reported significant growth reductions in the absence of visible injury at 660 $\mu g/m^3$ (0.25 ppm) SO_2 when the treatment sums of squares were partitioned. On the other hand, Heagle et al. (1974) also exposed Dare soybeans but found that plants exposed to 260 μg/m^3 (0.10 ppm) SO_2 6 hr/day for 133 days in closed field chambers failed to exhibit significant yield reductions, even in the presence of foliar injury.

Additional examples of ambiguities are found in some of the literature dealing with grasses. In a preliminary study, S 23 ryegrass exhibited significantly reduced growth when exposed to 310 μg/m^3 (0.12 ppm) SO_2 for 9 weeks or 0.067 ppm SO_2 for 26 weeks (Bell and Clough, 1973); however, the only foliar injury noted was a slight chlorosis and an enhanced rate of leaf senescence. Ashenden (1978) noted similar significant growth reductions for cocksfoot grass when exposed to 290 μg/m^3 (0.11 ppm) SO_2 for 4 weeks; reductions ranged from 32 to 52 percent for various yield parameters while foliar necrosis was only 5 percent. On the other hand, exposure of S 23 ryegrass to 50 or 370 μg/m^3 (0.02 or 0.14 ppm) SO_2 in two successive growth periods of 29 and 22 days was reported to result in foliar injury at the high concentration, but no yield effects at either concentration (Cowling and Koziol, 1978). Neither net photosynthesis nor dark respiration was significantly affected.

Different plant species differ in tolerance to SO_2 injury. Leaf injury and radial growth were evaluated on Douglas fir and ponderosa pine growing in nursery plots exposed to various doses of SO_2 in controlled fumigations to determine their tolerance to SO_2 exposure (Katz and McCallum, 1952). Slightly injured ponderosa pine (10 percent foliar symptoms) exhibited no significant deviations in growth while slightly injured Douglas fir (10 percent foliar symptoms) showed a definite growth retardation in comparison to control plants. The growth retardations were evident for 3 years after SO_2 exposure, followed by substantial recovery.

Sulfur dioxide concentrations have also been negatively correlated with annual ring width in Norway spruce (Keller, 1980). Exposures to 130, 260 and 520 μg/m^3 (0.05, 0.10, and 0.20 ppm) SO_2 were continuous for 10 weeks in the spring. Some injury was noted at (0.10) and 520 μg/m^3 (0.20 ppm), but a distinct decline of wood production was also found in cases where no visible injury occurred. When dormant seedlings of beech were exposed to the same SO_2 concentrations 130, 260 and 520 μg/m^3; (0.05, 0.10, and 0.20 ppm) for about 16 weeks, there was an increase in the number of terminal buds that failed to "break" in the spring for the 260 (0.10 ppm) and 520 (0.20 ppm) treatments (Keller, 1978).

The literature concerning SO_2-induced growth and yield effects and correlations with visible foliar injury is ambiguous. No studies consider all the potential variables that can affect plant response. This is a virtual impossibility for a single study and is especially true for field studies (which are most relevant for present purposes) where many environmental variables cannot be controlled. Also, many of the studies that have demonstrated adverse effects of SO_2 at low concentrations have utilized sensitive cultivars of plant species (which may or may not be representative of plant populations as a whole) and maintained exposure conditions conducive to maximum plant sensitivity. However, from the data available, we can conclude that growth and yield effects are not necessarily related to foliar injury. Depending upon the plant affected, the environmental conditions, and the pollutant exposure conditions, one may observe yield effects without injury, injury without yield effects, or positive associations between injury and yield.

5.1.9 Classification of Plant Sensitivity to Sulfur Dioxide

Limitations of space do not permit a listing here of all plants known to be sensitive to various doses of SO_2. Furthermore, in a listing of sensitive plants, the evidence collected should also indicate environmental, genetic, and cultural considerations that may in fact determine such sensitivities. In addition, general descriptions are difficult because plant responses to air pollutants vary at the genus, species, variety, and cultivar levels. Some listings of plants according to relative sensitivities have been prepared, however, using as a basis the expression of visible symptoms by any given plant. Injury expressed as losses in growth or yield, however, has generally not been considered in preparing such lists.

Jacobson and Hill (1970) published a list of plants sensitive to major phytotoxic air pollutants, and Linzon (1972) has classified 36 tree species as being either tolerant, intermediate, or sensitive to SO_2. These sensitivity lists do not identify the pollutant doses required to induce visible injury on indicator species. However, Jones et al. (1974) have published such details based upon observations over a 20-year period of 120 species growing in the vicinity of coal-fired power plants in the southeastern United States (Table 5-2).

Other compilations have also been presented, including that of Davis and Wilhour (1976) which provides information on an international basis, and the report of Hill et al. (1974) for vegetation native to the southwestern deserts of the United States.

Extensive efforts have been made to identify and develop certain sensitive plant species as potential bioindicators of ambient air SO_2 effects. Perhaps the most extensively examined plants for this use are eastern white pine (Pinus strobus) and numerous species of lichens. The literature on white pine has been reviewed by Gerhold (1977), and the most recent review discussing lichens as bioindicators was prepared by LeBlanc and Rao (1975). Other reports have been prepared mentioning the use of various ornamentals (Heggestad et al., 1973;

TABLE 5-2. SENSITIVITY GROUPINGS OF VEGETATION BASED ON VISIBLE INJURY AT DIFFERENT SO_2 EXPOSURES[a]

Sensitivity Grouping	SO_2 concentration $\mu g/m^3$ (ppm) and exposure time (hr)			Plants
	Peak[b]	1-hr	3-hr	
Sensitive:	2620-3930 $\mu g/m^3$ (1.0 - 1.5 ppm)	1310-2620 $\mu g/m^3$ (0.5 - 1.0 ppm)	790-1570 $\mu g/m^3$ (0.3 - 0.6 ppm)	Ragweeds Legumes Blackberry Southern pines Red and black oaks White ash Sumacs
Intermediate:	3930-5240 $\mu g/m^3$ (1.5 - 2.0 ppm)	2620-5240 $\mu g/m^3$ (1.0 - 2.0 ppm)	1570-2100 $\mu g/m^3$ (0.6 - 0.8 ppm)	Maples Locust Sweetgum Cherry Elms Tuliptree Many crop and garden species
Resistant:	>5240 $\mu g/m^3$ (> 2.0 ppm)	>5240 $\mu g/m^3$ (> 2.0 ppm)	>2100 $\mu g/m^3$ (> 0.8 ppm0	White oaks Potato Upland cotton Corn Dogwood Peach

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[a] Based on observations over a 20-year period of visible injury occurring on over 120 species growing in the vicinities of coal-fired power plants in the southeastern United States.

[b] Maximum 5 minute concentration.

Source: Jones et al., 1974.

Daessler et al., 1972; Pelz, 1962); bluegrass cultivars (Murray et al., 1975); scotch pine (Demeritt et al., 1971); hybrid poplar (Dochinger and Jensen, 1975); and trembling aspen (Karnosky, 1977).

Bioindicators for determining SO_2 effects must be used with caution, however, because other factors such as drought, nutrient imbalances, and other pollutants may induce injury symptoms that mimic those of SO_2. Therefore, several bioindicators should be used if any given geographic area is to be evaluated for possible SO_2 effects. In addition, individual species and more complicated plant bioindicator systems are not as effective in detecting SO_2 at low concentrations as are sophisticated instruments.

5.1.10 Dose-Response Relationships--Sulfur Dioxide

The primary focus of dose-response studies should be to delineate relationships between measurable indices of exposure dose and meaningful parameters of plant response. This section will examine such relationships both from the perspective of defining empirically demonstrated dose-response (or exposure effect) relationships based on our present knowledge and from the perspective of what generalizations might be reasonably made concerning likely effects of SO_2 on plants under ambient exposure conditions.

The dose (exposure dose) of SO_2 to which vegetation may be exposed is conventionally designated as the product of concentration in the plant's environment times the duration of exposure. The term exposure dose is a description of the amount of pollutant at the external plant surface. Response may be characterized by a measurable change in any parameter such as biochemical pathways, gas exchange rates, photosynthetic rates, physiological functions, degree of visibly recognizable leaf injury, or subsequent growth and yields. Plant responses may be beneficial or detrimental. They may also involve the expression of growth and yield effects without foliar symptoms or lead to overt symptoms that seldom become more serious than those associated with acute injury or chronic injury.

In interpreting dose-response studies wherein a measured plant response is correlated with exposure dose, it is important to realize that the relationship between exposure dose and the amount of pollutant entering the plant may be influenced significantly by environmental factors which control rates of pollutant flux into plant leaves and by plant factors that determine the metabolic fate of the pollutant within leaf tissues as noted earlier.

The role of short-term fluctuations in SO_2 may be particularly important where impacts of point sources are of concern (McLaughlin et al., 1976). Here concentrations may fluctuate widely during exposure, and damage to vegetation may be most closely associated with short-term averages (1 hr) or even brief peak concentrations (The term "peak" is not precise, but depends on instrumentation and the opinion of the scientist. However, a peak is usually of only a few minutes duration.) Consistent with this, laboratory experiments by Zahn (1970, 1961) have demonstrated the greater relative toxicity of short-term exposures at high concentrations of SO_2 than longer-term exposures with the same total exposure dose. Also, more recently McLaughlin et al. (1979) studied the effects of varying the peak-to-mean SO_2 concentration ratio on kidney beans in short-term (3 hr) exposures to SO_2. They found that increasing the peak-to-mean ratio from 1.0 (steady state exposure at 0.50 ppm for 3 hours) to 2.0 (3 hr exposure with peak = 2620 $\mu g/m^3$ or 1.0 ppm) did not alter post fumigation photosynthetic depression. Further increasing the ratio to 6.0 (1 hour exposure with peak = 5240 $\mu g/m^3$ or 2.0 ppm), however, tripled the postfumigation photosynthetic depression. Total dose delivered in the three exposures was 1.5, 1.8, and 1.1 ppm hr, respectively. Clearly the quantity of SO_2 to which the plants are exposed may have a very different effective potential as the parameters of the exposure are changed.

Another important aspect of exposure dose is the frequency and duration of periods of low SO_2 stress. Zahn (1970) emphasized that periods of low SO_2 concentration may be critical to the recovery potential of plant systems following exposure to elevated levels of SO_2. Thus, continuous exposure systems probably overestimate the toxicity of the delivery dose in many cases because physiological recovery is not permitted. Such recovery would be expected under most exposure regimes in the field where fluctuating synoptic or local meteorological conditions strongly influence exposure patterns.

Equally critical in defining the biologically significant features of exposure regimes is a description of the significant parameters of plant response. In interpreting or predicting plant response to SO_2, it is important to keep in perspective the fact that plant growth and development represents an integration of cellular and biochemical processes, just as community behavior is an integration of the performance of component species. The internal allocation of resources (carbon, water, and nutrients) to growth is an integrative and, in many cases, resilient process that plays a major role in determining how both individual plants and plant communities respond to environmental stress (McLaughlin and Shriner, 1980). The fact that a response is measured following exposure to a given dose of SO_2 may be of interest in understanding the mechanism of action and in identifying the biologically significant features of dose; however, it does not necessarily mean that an effect will be measured at a subsequent higher level of plant organization. Responses at higher levels of plant organization, however, must be viewed within the perspective of the increasingly complex biotic and abiotic factors that control plant response and influence our attempts to move the focus of our studies from processes to plants and from plants to communities. These factors similarly limit our capacity to extend experimental protocols beyond the confines of our carefully controlled laboratory studies to more natural, and more variable, field situations.

Several attempts have been made to characterize dose-response relationships in a mathematical sense using monitored concentrations, exposure times, and injury thresholds as modified by physical and biotic factors expressed as constants (Zahn, 1963a,b; Thomas and Hill, 1935; O'Gara, 1922). However, their consistency and usefulness are limited by numerous physical and biotic factors that must be considered in evaluating dose-response data. Changes in exposure conditions, differences in exposure methodology and efficiency of monitoring equipment, and consistency of measurements within a study and between studies on the same plant will directly influence results.

Relatively few crops of economic importance have been studied under field conditions. Results obtained for SO_2 exposure effects on yields for certain commercially important species are summarized in Table 5-3. (Statistical significances are noted in the table.) Of the results listed, those for soybeans, wheat and barley are economically the most important. For soybeans, single 4.33 hr exposures to 3670, 4450, or 5240 $\mu g/m^3$ (1.4, 1.7, or 2.0 ppm) SO_2 induced 4.5, 11, and 15 percent yield decreases, respectively. Also, 5.2 to 15 percent yield losses in soybean cv. Wells were observed with intermittent exposures to 0.09 to 0.36 ppm SO_2 for an average fumigation period of 4.2 hours on 18 different days scattered from July 19 through August 27 of the soybean growing season (Sprugel et al., 1980). A greater yield loss (20.5 to 45 percent) resulted when soybeans were exposed to 4.7 hours of SO_2 at 790, or 2070 $\mu g/m^3$ (0.30 or 0.79 ppm) on 24 different days scattered through the soybean growing season using the ZAPS exposure approach in an attempt to approximate ambient

TABLE 5-3. EFFECTS OF EXPOSURE TO SO_2 ON PLANTS UNDER FIELD CONDITIONS*

Plant species	Type of exposure	Time	Concentration µg/m³	(ppm)	Effects	References
Soybeans	P	4 1/3 hrs	3670	(1.4)	4.5% loss in yield (N.S.)	Miller et al. 1979
Soybeans	P	4 1/3 hrs	4450	(1.7)	11% loss in yield**	
Soybeans	P	4 1/3 hrs	5240	(2.0)	15% loss in yield*	
Soybeans cv Wells	I	4.2 hrs × 18 exposures	240	(0.09)	6.4% yield loss**	Sprugel et al. 1980 and Miller et al. 1980
Soybeans cv Wells	I	4.2 hrs × 18 exposures	260	(0.10)	5.2% yield loss*	
Soybeans cv Wells	I	4.2 hrs × 18 exposures	500	(0.19)	12.2% yield loss**	
Soybeans cv Wells	I	4.2 hrs × 18 exposures	660	(0.25)	19.2% yield loss**	
Soybeans cv Wells	I	4.2 hrs × 18 exposures	940	(0.36)	15.9% yield loss**	
Soybeans cv Wells	I	4.7 hrs × 24 exposures	310	(0.12)	12.3% yield loss**	
Soybeans cv Wells	I	4.7 hrs × 24 exposures	790	(0.30)	20.5% yield loss**	
Soybeans cv Wells	I	4.7 hrs × 24 exposures	2070	(0.79)	45.3% yield loss**	
Soybeans cv Dare	I	6 hrs/day for 43-92 and 133 days	260	(0.10)	No effect until 92nd day, 12% defoliation (N.S.)	Heagle et al. 1974
Wheat	I	3 hrs × 8 exposures/growing season	100	(0.04)	No yield effect*	Sij et al. 1974
Wheat	I	3 hrs × 7 exposures/growing season	1180	(0.45)	No yield effect*	
Spring Wheat	I	3 hrs × 3 exposures/growing season	660-3140	(0.25-1.20)	No yield effect	Wilhour et al. 1978
Spring Wheat	I	3 hrs × 7 exposures/growing season	660-3140	(0.25-1.20)	No yield effect	
Spring Wheat	I	72 hrs/wk/growing season	80- 260	(0.03-0.10)	No yield effect	
Spring Wheat	I	72 hrs/wk/growing season	390	(0.15)	No yield effect	
Durum Wheat	I	3 hrs × 3 exposures/growing season	660-3140	(0.25-1.20)	No yield effect	Wilhour et al. 1978
Durum Wheat	I	3 hrs × 7 exposures/growing season	660-3140	(0.25-1.20)	No yield effect	
Durum Wheat	I	72 hrs/wk/growing season	80- 260	(0.03-0.10)	No yield effect	
Durum Wheat	I	72 hrs/wk/growing season	390	(0.15)	42% yield loss (N.S.)	

TABLE 5-3. (continued)

Plant species	Type of exposure	Time	Concentration (ppm)	Effects	References
Barley	I	3 hrs × 3 exposures/ growing season	660-3140 (0.25-1.20)	No yield effect	Wilhour et al. 1978
Barley	I	3 hrs × 7 exposures/ growing season	660-3140 (0.25-1.20)	No yield effect	
Barley	I	72 hrs/wk/growing season	80- 260 (0.03-0.10)	No yield effect	
Barley	I	72 hrs/wk/growing season	390 (0.15)	44% yield loss (N.S.)	
Alfalfa	I	3 hrs × 3 exposures/ growing season	660-3140 (0.25-1.20)	No yield effect	Wilhour et al. 1978
Alfalfa	I	3 hrs × 7 exposures/	660-3140 (0.25-1.20)	No yield effect	
Western Wheat Grass	C	growing season	50-260 (0.02-0.10)[a]	Increasing S content with increasing SO_2	Dodd et al., 1978
Prairie June Grass	C	growing season	50-260 (0.02-0.10)[a]	Significant decrease in digestible protein	

P = Peak (short-term, 8 hrs or less), I = intermittent and C = continuous exposure.

*Statistically significant change at $P < 0.05$.

**Statistically significant change at $P < 0.01$.

N.S. Results were not significant at $P < 0.05$ probability level.

[a] Values are for a geometric mean.

conditions. The latter of the intermittently repeated exposures at 790 and 2070 μg/m^3 (0.30 and 0.79 ppm), therefore, appeared to have a detrimental yield effect as great or greater than single exposures of 5240 μg/m^3 (2.0 ppm) for 4 1/3 hours.

In contrast to effects reported by Sprugel et al. (1980) at 240 and 2620 μg/m^3 (0.09 and 0.10 ppm) SO_2, Heagle et al. (1974) exposed the soybean cv. Dare in closed top chambers in the field for 6 hours per day at 260 μg/m^3 (0.1 ppm) SO_2 for 133 days and noted little effect other than defoliation. The contrasting results may be due to cultivar (Wells vs. Dare) differences. Or, as Sprugel et al. (1980) suggest, the difference in results could be due to differences in the exposure systems. The closed field chamber of Heagle et al. (1974) may have modified the macroenvironment of the plants being exposed, whereas with the open-air ZAPS system occasional high peak exposures may result. One such peak of 2100 μg/m^3 (0.8 ppm) SO_2 for one 2-minute sample was measured in 1977. Thus, the reductions in yield seen in the Sprugel et al. (1980) studies could have been due to the peaks rather than the general mean. Peaks of this type, however, are not unusual but rather are typical of air pollution episodes, particularly near point sources. Another possible factor is that in the ambient air there is a possibility of synergistic interactions. Such interactions with ozone may have increased the effects of SO_2 in the Sprugel et al. (1980) study. In 1977, ozone concentrations in the field were monitored during the first part of the season and averaged between 130 and 160 μg/m^3 (0.05 and 0.06 ppm) during the fumigations and on at least two occasions, the concentrations exceeded 260 μg/m^3 (0.1 ppm) for one hour or more. Sprugel et al. (1980), however, point out that the study of Heagle et al. (1974) produced no evidence for greater than additive effects of SO_2/O_3 on soybeans. Again, the conditions in the field under which the soybeans were exposed using the

ZAPS system probably more nearly simulate those under which field grown crops would normally be exposed and the ZAPS results rather clearly indicate that repeated 4.7 hr. exposures to $\geq$790 μg/m^3 ($\geq$0.30 ppm) SO_2 during the growing season markedly reduced (by >20 percent) soybean yields under the conditions prevailing during the study.

As for other commercially important crop species, neither spring wheat or Durum wheat exhibited significant yield loss effects when exposed to intermittent concentrations of SO_2 from 660 (0.25) up to 3140 μg/m^3 (1.2 ppm), 3 times or 7 times over the growing season. When concentrations of 80 (0.03) to 390 μg/m^3 (0.15 ppm) for 72 hours per week were used for the growing season these intermittant exposures resulted in no significant yield loss effects. Barley responded in the same manner as Durum wheat, showing no significant response at any of the SO_2 concentrations or exposure times. Similar statements can be made regarding the results of repeated 3 hr 660 (0.25) to 3140 μg/m^3 (1.20 ppm) SO_2 exposures of alfalfa noted in Table 5-3 (Wilhour et al., 1978).

A few major investigations of the effects of SO_2 on vegetational species growing under natural conditions have been reported (Legge et al., 1981; Legge, 1980; Linzon, 1980; Vins and Mrkva, 1973; Linzon, 1971; Dreisinger and McGovern, 1970; Materna et al., 1969; Dreisinger, 1965). Table 5-4 illustrates the degree of injury to eastern white pines (Pinus strobus) observed over a 10-year period (1953-1963) in the sulfur fume effects area of smelters near Sudbury, Ontario, Canada (Linzon, 1971). Linzon (1978, 1971) has indicated that a pollution (SO_2) gradient existed within the designated study area and effects correlated well with this gradient. Chronic effects on forest growth were prominent where SO_2 air concentrations annually averaged 45 or 115 μg/m^3 (0.017 or 0.045 ppm) SO_2, and such effects were not reported in areas receiving 21 μg/m^3 (0.008 ppm) SO_2 annually. Although monitoring of SO_2 was conducted in these studies, neither

TABLE 5-4. THE DEGREE OF INJURY OF EASTERN WHITE PINE OBSERVED AT VARIOUS DISTANCES FROM THE SUDBURY SMELTERS FOR 1953-63

Forest Sampling Station[a] (Distance and Direction from Sudbury)	Trees with Current Year's Foliage Injured in August 1963 (%)	Trees with 1-Year-Old (1962) Foliage Injured		Trees with 2-Year Old Foliage		Net Annual Average Gain or Loss in Total Volume, 1953-1963 (%)	Annual Average Mortality 1953-1963 (%)	Degree of SO_2 Damage	Average SO_2 Concentration[b] for Total Measurement Period 1954-1963 μg/m³ (ppm)
		June 1963 (%)	August 1963 (%)	Injured in June 1963 (%)	Lacking in August 1963 (%)				
West Bay (19 miles NE)	2.0	38.0	77.9	96.0	20.6	-1.3	2.6	Acute and chronic injury	115 (0.045)
Portage Bay (25 miles NE)	1.1	21.5	55.6	77.0	15.2	-0.5	2.5	Mostly chronic and little acute injury	45 (0.017)
Grassy to Emerald Lake (40-43 miles NE)	0.4	2.5	16.7	37.5	9.1	+1.8	1.4	Very little chronic injury	21 (0.008)
Lake Matinenda (93 miles W)	0.6	0.3	2.1	10.1	3.9	+2.1	0.5	Control: no SO_2 injury	3 (0.001)[c] (Sturgeon Falls)
Correlation Coefficient (r)	0.96	0.96	0.93**	0.90**	0.94**	0.90**	0.81		

[a] Linzon (1971) (Pollutants other than SO_2 were not measured and the monitoring was done several miles from the pine stands.)

[b] Dreisinger (1965)

[c] Data for 5-month growing season-1971

*$p < 0.05$

**$p < 0.10$

concentrations of other air pollutants nor their potential effects were evaluated by the authors. It is also not clear to what extent high short-term peak SO_2 exposures may have contributed to the effects reported to be associated with these annual average SO_2 concentrations.

Ambient air exposures to sulfur dioxide that caused injury to a variety of both sensitive and non-sensitive species of vegetation are shown in Table 5-5. The data listed in the table were derived from the work of Dreisinger and McGovern (1970) and has been previously reviewed and cited in EPA's Revised Chapter 5 for Air Quality Criteria for Sulfur Oxides (U.S. Environmental Protection Agency, 1973) and the National Academy of Sciences' report on Sulfur Oxides (NAS, 1978). In addition, air quality data from the work have been analyzed and discussed by Linzon (1971). As presented and concluded by Dreisinger and McGovern in their work and cited in the NAS report, "one could be reasonably certain of avoiding foliar injury to vegetation in the study area if concentrations did not exceed 1830, 1050, 680 or 470 $\mu g/m^3$ (0.70, 0.40, 0.26, or 0.18 ppm) as 1-, 2-, 4-, or 8-h means, respectively."

These conclusions appear to be based on the following discussion in the Dreisinger and McGovern (1970) paper:

> "What levels of sulphur dioxide are considered potentially injurious to vegetation? It was shown in previous reports (Dreisinger, 1965, 1967) that most of the injury to vegetation that occurred near recorder stations in the Sudbury area happened when concentrations and durations of sulphur dioxide reached or exceeded the following levels during the day time.
>
> 0.95 ppm for 1 hour)
> or 0.55 ppm for 2 hours)
> or 0.35 ppm for 4 hours) Intensity factor of 100
> or 0.25 ppm for 8 hours)
>
> "It is not true that injury always occurs when these levels are reached or exceeded. Whether or not damage actually happens depends, to a large extent, on the environmental conditions prevailing at the time of the fumigation. There have been occasions in the Sudbury area when levels, two, three, and even four times those listed above were recorded and no injury occurred. Those fumigations simply happened at times when vegetation was resistant."

TABLE 5-5. AMBIENT EXPOSURES TO SULFUR DIOXIDE THAT CAUSED INJURY TO VEGETATION[a]

Exposure where injured SO_2 Concentration, µg/m³ (ppm) for averaging periods of:				Plant
1 h	2 h	4 h	8 h	
1070 (0.41)	1000 (0.38)	860 (0.33)	790 (0.30)	Willow
1070 (0.41)	1000 (0.38)	890 (0.34)	680 (0.26)	Larch
1100 (0.42)	1020 (0.39)	680 (0.26)	340 (0.13)	Quaking aspen
1180 (0.45)	890 (0.34)	660 (0.25)	550 (0.21)	Bracken fern
1180 (0.45)	920 (0.35)	660 (0.25)	550 (0.21)	White pine
1210 (0.46)	1000 (0.38)	730 (0.28)	550 (0.21)	White birch
1210 (0.46)	1180 (0.45)	1130 (0.43)	550 (0.21)	Bean
1210 (0.46)	1130 (0.43)	1130 (0.43)	550 (0.21)	Alder
1360 (0.52)	1150 (0.44)	760 (0.29)	520 (0.20)	Jack pine
1470 (0.56)	1020 (0.39)	680 (0.26)	390 (0.15)	Buckwheat
1650 (0.63)	1150 (0.44)	630 (0.24)	310 (0.12)	Barley
1650 (0.63)	1550 (0.59)	890 (0.34)	450 (0.17)	Oats, peas, rhubarb
1680 (0.64)	1470 (0.56)	1130 (0.43)	1000 (0.38)	Lettuce, tomato, potato
1730 (0.66)	1130 (0.43)	970 (0.37)	520 (0.20)	Large-toothed aspen
1730 (0.66)	1180 (0.45)	1150 (0.44)	860 (0.33)	Austrian pine
1730 (0.66)	1410 (0.54)	1050 (0.40)	550 (0.21)	Timothy
1830 (0.70)	1210 (0.46)	710 (0.27)	370 (0.14)	Red clover
1830 (0.74)	1650 (0.63)	1390 (0.53)	1020 (0.39)	Raspberry
1990 (0.76)	1410 (0.54)	760 (0.29)	370 (0.14)	Radish
2040 (0.78)	1810 (0.69)	1150 (0.44)	790 (0.30)	Red pine
2150 (0.82)	1700 (0.65)	1180 (0.45)	680 (0.26)	Balsam poplar
2150 (0.82)	1700 (0.65)	1620 (0.62)	1210 (0.46)	Sugar maple
2280 (0.87)	1940 (0.74)	1440 (0.55)	760 (0.29)	Celery
2280 (0.87)	2070 (0.79)	1830 (0.70)	1310 (0.50)	White spruce
2310 (0.88)	1680 (0.64)	1100 (0.42)	710 (0.27)	Swiss chard
2330 (0.89)	2150 (0.82)	1600 (0.61)	1070 (0.41)	Red oak
2460 (0.94)	2330 (0.89)	1830 (0.70)	1180 (0.45)	Cabbage
2830 (1.08)	2070 (0.79)	1310 (0.50)	660 (0.25)	Carrot, cucumber
2990 (1.14)	1970 (0.75)	1180 (0.45)	600 (0.23)	Witch hazel
3430 (1.31)	2020 (0.77)	1180 (0.45)	600 (0.23)	Beet, turnip
3510 (1.34)	2380 (0.91)	1310 (0.50)	890 (0.34)	Spinach

[a] Derived from Dreisinger and McGovern, and reprinted from NAS Sulfur Oxides Document, 1978, p. 6-29.

> "Conversely, on occasions, some very sensitive species were injured with levels approximately 25% less than the above. In each case the injury occurred during June or July, which, for the Sudbury area, are the months when the most rapid growth of vegetation takes place. Hot, humid weather prevailed in most cases, producing conditions extremely favourable for a high photosynthetic rate and in turn increased susceptibility to sulphur dioxide."
>
> "The occasions, whoever, when this happened, were quite rare, only nine times in a ten-year period, and the injury that did result was not extensive so that for all intents and purposes, it is only when all SO_2 levels reach the 100-intensity mark or more that the potential for wide-spread injury is present."

The general conclusions of Dreisinger and McGovern (1970) have essentially been reinforced by McLaughlin (1981) and Jones et al. (1974).

McLaughlin (1981), although recognizing that especially in arid regions of the U.S. many species of vegetation would not be visibly injured even in some cases by SO_2 concentrations of 11 ppm for 2 hours as suggested by Hill et al (1974), focused on a subset of vegetational species in the more hot and humid Southeast which he believed to represent a spectrum of plant response ranging from sensitive to tolerant (McLaughlin and Lee, 1974). McLaughlin concluded that 20 percent of the selected species would show visible injury at peak (5 minutes), 1-, and 3-hour concentrations of 3140, 1700, and 920 $\mu g/m^3$ (1.20, 0.65, and 0.35 ppm), respectively.

Jones et al. (1974) also reported, as previously presented in Table 5-2, the wide range in SO_2 concentrations that at peak (maximum of 5 minutes), 1-, and 3-hour time periods injured different species of plants that were classified as sensitive, intermediate, or resistant to SO_2 exposures. However, because of the many randomly occurring environmental factors affecting injury, e.g., plant resistance, temperature, moisture, etc., Jones (1981) recommended that an analysis of probability of injury occurrence should be applied prior to any generalizations regarding the specific concentration of SO_2 causing plant injury.

The work of Hill et al. (1974) also reinforces the widely accepted statement by Dreisinger and McGovern (1970) that hot, humid weather produces conditions extremely favorable for increased plant susceptibility to sulfur dioxide.

The studies of Vins and Mrkva (1973) and Materna et al. (1969), although reporting foliar and growth increment losses in forest trees as being due to SO_2, were conducted in areas of fluoride contamination or used only sporadic monitoring schedules, respectively. Pollution gradients were evident and SO_2 exposure was probably involved, but conclusive proof of losses attributed to SO_2 was not presented as it was for the Sudbury area.

The effects of exposing seedling tree species to SO_2 levels within or approaching the ambient range are summarized in Table 5-6. Concentrations of greater than 660 μg/m^3 (0.25 ppm) SO_2 for 2 hours were required to induce slight injury to several pine species (Berry, 1971), but overall trends for increasing foliar injury do not follow increasing dose for conifers per se. Smith and Davis (1978) exposed several conifers (pine, spruce, fir and Douglas fir) to doses of 2620 μg/m^3 (1.0 ppm SO_2) for 4 hours or 2.0 ppm SO_2 for 2 hours and only the pines developed necrotic tips at the 5240 μg/m^3 (2.0 ppm) dose. However, studies done with tree seedlings under artificial conditions are difficult to extrapolate to expected yield loss effects under field conditions. Of the studies reviewed and accepted without caveats, none demonstrated significant height or annual increment growth effects.

In an evaluation of SO_2 effects on photosynthesis, Keller (1977) used field chambers to expose potted white fir, Norway spruce and Scotch pine to 3 concentrations of SO_2 (130, 260 and 520 μg/m^3 and a control of 0.0 μg/m^3, 0.05, 0.10, and 0.20 ppm) for 10 weeks each during the spring, summer, and fall, respectively. Several types of photosynthetic response rates were obtained; however, trends of decreasing rate occurred as exposures increased especially when

TABLE 5-6. SUMMARY OF THE EFFECTS RESULTING FROM THE EXPOSURE OF SEEDLING TREE SPECIES IN THE LABORATORY*

Plant species	Type of exposure	Time	Concentration μg/m³ (ppm)	Effects	References
Scotch Pine	P	1 hr-6 hrs	1310-5240 (0.5-2.00)	Foliar injury - except at 5 hrs at 0.5 ppm	Smith and Davis, 1978
Eastern White Pine	P	2 hrs - 6 hrs	6.6-1310 (0.025-0.5)	Foliar injury even on tolerant clones at 6 hrs at 0.15 ppm	Houston, 1974
Red Pine	P	2 hrs	660 (0.25)		Berry, 1972
Loblolly Pine	P	2 hrs	660 (0.25)		
Shortleaf Pine	P	2 hrs	660 (0.25)	Foliar injury; most sensitive period of plant 8-10 wks	Berry, 1972
Virginia Pine	P	2 hrs	660 (0.25)		
Slash Pine	P	2 hrs	660 (0.25)		
Jack Pine	P	2 hrs	660 (0.25)	Foliar injury	Berry, 1974
Jack Pine	P	24 hrs	470-520 (0.18-0.2)	Inhibition of foliar lipid synthesis; inhibition reversable	Malhotra and Kahn, 1978
Balsam Fir	P	2, 4, 5 hrs	5240, 2620 and 1310 (2.0, 1.0 and 0.5)	Foliar injury only at 4 hrs, then less than 4%	
Fraser Fir	P	2, 4, 5 hrs	5240, 2620 and 1310 (2.0, 1.0 and 0.5)	Foliar injury only at 4hrs, then less than 4%	
White Fir	P	2, 4, 5 hrs	5240, 2620 and 1310 (2.0, 1.0 and 0.5)	Foliar injury only at 4 hrs, then less than 4%	
Blue Spruce	P	2, 4, 5 hrs	5240, 2620 and 1310 (2.0, 1.0 and 0.5)	Foliar injury only at 4 hrs, then less than 4%	Smith and Davis, 1978
Douglas Fir	P	2, 4, 5 hrs	5240, 2620 and 1310 (2.0, 1.0 and 0.5)	Foliar injury only at 4 hrs, then less than 4%	
Austrian Pine	P	2, 4, 5 hrs	5240, 2620 and 1310 (2.0, 1.0 and 0.5)	Foliar injury except at 4 hrs and 0.5 ppm	
Ponderosa Pine	P	2, 4, 5 hrs	5240, 2620 and 1310 (2.0, 1.0 and 0.5)	Foliar injury except at 5 hrs and 0.5 ppm	
Ponderosa Pine	P	9 hrs/days × 8 wks	1180 (0.45)	Tip necrosis	Evans and Miller, 1975
American Elm	P	6 hrs	5240 (2.0)	Severe foliar injury, defoliation	Constantinidou and Kozlowski, 1979a
American Elm	P	8 hrs	2620 (1.0)	Inhibited stomatal closing	Noland and Kozlowski, 1979

TABLE 5-6. (continued)

Plant species	Type of exposure	Time	Concentration µg/m³ (ppm)	Effects	References
American Elm	C	12 hrs	5240 (2.0)	Stomatal closing induced, increases content when plants fumigated in light	Temple, 1972
Chinese Elm	P	6 hrs	5240 (2.0)	100% leaf necrosis	Temple, 1972
Chinese Elm	C	24 hrs/day for 30 days	1310 (0.5)	7 days for chlorosis	Temple, 1972
Gingko	P	6 hrs	7900 (3.0)	50% leaf necrosis	Temple, 1972
Gingko	C	24 hrs/day for 30 days	1310 (0.5)	14 days for chlorosis	Temple, 1972
Trembling Aspen	P	3 hrs	920; 1700 (0.35; 0.65)	Foliar injury; 2% and 2.3%	Karnosky, 1976
Sugar Maple	C	24 hrs/day for 1 wk	1310 (0.5)	54% reduction in photosynthesis	
Sugar Maple	I	4 hrs/day for 3 wk	1310 (0.5)	43% reduction in photosynthesis	
Black Oak	C	24 hrs/day for 1 wk	1310 (0.5)	48% reduction in photosynthesis	
Black Oak	I	4 hrs/day for 3 wk	1310 (0.5)	74% reduction in photosynthesis	Carlson, 1979
White Ash	C	24 hrs/day for 1 wk	1310 (0.50)	20% reduction in photosynthesis	
White Ash	I	4 hrs/day for 3 wk	1310 (0.50)	7% reduction in photosynthesis	
Norway Maple	C	24 hrs/day for 30 days	1310 (0.50)	12 days for chlorosis	Temple, 1972
Pin Oak	C	24 hrs/day for 30 days	1310 (0.50)	30 days for chlorosis	Temple, 1972
Norway Spruce	C	10 wks	1310 (0.05)	No foliar injury, 25% < volume	Keller, 1980
Norway Spruce	C	10 wks	260 (0.10)	Foliar injury 38% < volume	Keller, 1980
Norway Spruce	C	10 wks	520 (0.20)	Foliar injury 53% < volume	Keller, 1980
Beech Spruce	C	16 wks	130 (0.05)	A few buds killed	Keller, 1978
Beech Spruce	C	in winter	260 (0.10)	Many buds killed	Keller, 1978
Beech Spruce	C		520 (0.20)	50% buds killed	Keller, 1978

*Data for this table comes from Table 8A-3 in Appendix 8A.

P, C, and I indicate peak (short-term average for 8 hrs or less), continuous and intermittent exposures.

administered during the 10-week period in the spring. Effects were less during the summer and fall exposure periods and spruce responded positively to SO_2 exposures of 130 μg/m^3 (0.05 ppm) during the initial part of the fall period. Keller (1977) also reported that even with the most severe depression of photosynthesis, there were no visible foliar symptoms in evidence. Keller (1980) utilized a similar exposure system and SO_2 doses to study effects to the annual ring width in two clones of Norway spruce. He reported significantly depressed CO_2 uptake with higher doses (260 and 520 μg/m^3; 0.10 and 0.20 ppm SO_2, 10 weeks), but only a trend was noted for the 0.05 ppm SO_2 treatment; visible symptoms and trends of reduced cambial growth occurred at only the higher dose.

Based on the limited data available concerning nonwoody components of native ecosystems, there appear to be no adverse yield effects below 160 μg/m^3 (0.06 ppm) SO_2 for 6 weeks. Most of the acceptable literature deals with long-term (several weeks) SO_2 exposures well above ambient atmosphere concentrations. There is some indication of beneficial yield effects below 160 μg/m^3 (0.06 ppm) SO_2 on one species (i.e., Indian ricegrass). As stated previously in Section 5.1.5, low doses of SO_2 may increase of productivity of certain crops. Concentrations of 80-160 μg/m^3 (0.03 to 0.06 ppm) continuously for 6 weeks of exposure increased the productivity of desert grass by 8 percent over the control plants which were grown in indigenous soils (Ferenbaugh, 1978). Other studies have also demonstrated beneficial effects, but experimental conditions included a sulfur-deficient growing medium.

More definitive dose-response studies both with and without the addition of other pollutants are needed before the biologically significant features of typical regional exposure regimes can be positively delineated. The National Crop Loss Assessment Network (NCLAN), which has only recently begun its studies, is a step in this direction.

5.2 EFFECTS OF MIXTURES OF SO_2 AND OTHER POLLUTANTS ON AGROECOSYSTEMS

Ambient atmospheres usually contain more than one pollutant. Atmospheric monitoring of long-distance transport of photochemical oxidants and oxidant precursors (Husar et al., 1978; U.S. EPA, 1971), and the presence of acidic precipitation over large areas of the eastern United States (Cogbill, 1976) have documented the fact that emissions from specific sources are mixed with ambient concentrations of one or more pollutants. Extrapolation from results of single pollutant effects on vegetation under ambient field conditions must be approached with caution because reactions to pollutant combinations under controlled conditions, the interaction of constantly changing environmental factors, and fluctuating pollutant doses must also be evaluated before a conclusive statement of the importance of such interactions can be made. Reinert (1975) and Reinert et al. (1975) have prepared the most recent reviews of this area of investigation. Some examples of the available literature follow.

5.2.1 Sulfur Dioxide and Ozone

A more-than-additive reaction on vegetation was first reported for ozone and SO_2 (Menser and Heggestad, 1966). Tobacco was severely injured by 80 $\mu g/m^3$ (0.03 ppm) ozone and 630 $\mu g/m^3$ (0.24 ppm) SO_2 when the pollutants were combined for either 2 or 4 hours, whereas when used alone neither pollutant produced foliar symptoms.

Since that first report, the effects of mixtures of ozone and SO_2 have been studied using a variety of plant species. Radish and alfalfa plants showed more-than-additive foliar injury after a 4-hr exposure to a mixture of 200 $\mu g/m^3$ (0.10 ppm) O_3 + 260 $\mu g/m^3$ (0.10 ppm) SO_2 (Tingey et al., 1973a), but less-than-additive growth reduction (top and root weights) from an 8 hr/day, 5 day/wk, 5-week exposure of radish (alfalfa total exposure time unknown) to a mixture of 100 $\mu g/m^3$ (0.05 ppm) O_3 + 130 $\mu g/m^3$ (0.05 ppm) SO_2 (Tingey and

Reinert, 1975; Tingey et al., 1971a). Greater-than-additive foliar injury effects have also been reported for broccoli and tobacco, while additive or less-than-additive effects have been noted for cabbage, tomato, lima bean, bromegrass, spinach, onion, and soybean (Tingey et al., 1973a). Soybean has exhibited insignificant less-than-additive foliar injury effects (Tingey et al., 1973a) while exhibiting significantly greater-than-additive growth effects (Tingey et al., 1973b).

Most researchers examining the effects of pollutant mixtures have utilized standard means comparisons to express the responses. These tests usually do not adequately evaluate the interaction: the failure of one pollutant to be consistent at different concentrations of the second pollutant. Reinert and Nelson (1980) used sums of squares partitioning by factorial analysis to examine the effects of 1310 $\mu g/m^3$ (0.5 ppm) SO_2 and 490 $\mu g/m^3$ (0.25 ppm) O_3 (4-hr exposures, 4 times, 6 days apart) on Begonia. A significantly less-than-additive effect was found for flower weight in 1 of 5 cultivars. The same technique was utilized by Reinert and Weber (1980) to evaluate the effects of 490 $\mu g/m^3$ (0.25 ppm) O_3 and 660 $\mu g/m^3$ (0.25 ppm) SO_2 (exposed 4 h/day, 3 days/wk, for 11 wks) on soybean (Dare); an additive effect of the pollutant mixture was demonstrated.

Field-grown soybeans (cv. Dare) exposed to 200 $\mu g/m^3$ (0.10 ppm) O_3 alone or 200 $\mu g/m^3$ (0.10 ppm) O_3 + 260 $\mu g/m^3$ (0.10 ppm) SO_2 for 6 hr/day for 133 days in field chambers exhibited injury and defoliation. Due to the mixture, injury and yield were increased (9 percent) and decreased (19 percent), respectively, when compared to the ozone-alone treatment, but the differences were not significant (Heagle et al., 1974). Two cultivars of bean exposed to sulfur dioxide and ozone showed interactive effects between these two gases, but the magnitude and direction of the effects depended on the cultivar and on the pollutant concentrations (Jacobson and Colavito, 1976).

Many studies have been conducted on the effects of mixtures of sulfur dioxide and ozone on eastern white pine (Pinus strobus L.) (Houston, 1974; Costonis, 1973; Houston and Stairs, 1973; Dochinger and Heck, 1969). Genetic control of sulfur dioxide and ozone tolerance in this species has been demonstrated for low concentrations of SO_2 (66 $\mu g/m^3$ 0.025 ppm) and O_2 (100 $\mu g/m^3$ 0.05 ppm) for only 6 hr with consistent injury to the exposed sensitive clones (Houston and Stairs, 1973). Houston (1974) later used mixtures of sulfur dioxide and ozone at concentrations simulating actual field conditions and reported that even the lowest concentrations of O_3 (100 $\mu g/m^3$ 0.05 ppm) and SO_2 (130 $\mu g/m^3$ 0.05 ppm) for 6 hr in mixture caused more serious damage than that resulting from either pollutant alone at similar concentrations. A less-than-additive effect on foliar injury was noted when Scotch pine trees were exposed to 660 $\mu g/m^3$ (0.25 ppm) SO_2 and/or 270 $\mu g/m^3$ (0.14 ppm) or 570 $\mu g/m^3$ (0.29 ppm) O_3, 6 hr/day for varying time periods (Neilson et al., 1977).

Exposure of aspen clones to 100 $\mu g/m^3$ (0.05 ppm) O_3 and/or 520 $\mu g/m^3$ (0.20 ppm) SO_2 for 3 hr resulted in a more than additive number of plants in the mix exhibiting foliar injury (Karnosky, 1976).

Oshima (1978), using enclosed, round chambers in which the air was constantly stirred, conducted a field experiment to assess the effect of SO_2 on the yield of red kidney beans, Phaseolus vulgaris, grown in pots. The beans were exposed to 260 $\mu g/m^3$ (0.10 ppm) of SO_2 for 6 hr/day for a total of 335 hours and at the same time were exposed to a gradient of ozone doses. The ozone concentrations were those that resulted when ambient air at Riverside, California, was passed directly into the chamber or when 25, 50, 75 and 100 percent of the air was passed through a charcoal filter. The temperature, light, and humidity approximated that of ambient air. Plants were in the chambers for a total of 78 days. An interaction with ozone and SO_2 was documented in the 50 percent carbon filtered treatment (51.44 ppm-hrs) and produced a significant reduction in yield (37 percent) and plant biomass. The data also suggested the possibility of an interaction in the 75 percent filtered treatment (28.22 ppm-hrs) in that yield was reduced 17 percent, but this reduction was not significant (p = 0.20 level). Sulfur dioxide alone at 260 $\mu g/m^3$ (0.10 ppm) did not produce detectable plant or yield responses and did not have an interactive effect at ozone doses exceeding 51.44 ppm-hrs.

5.2.2 Sulfur and Nitrogen Dioxide

The occurrence of SO_2 and nitrogen dioxide (NO_2) in the atmosphere has been associated with power plant plumes as well as mobile sources. However, ambient concentrations of NO_2 seldom reach the injury threshold, and the literature for NO_2 suggests that any injury associated with NO_2 results from interactions with other pollutants (Jacobson and Hill, 1970).

No injury occurred to oats, beans, soybeans, radish, tomato, or tobacco following exposure for 4 hr to up to 3760 $\mu g/m^3$ (2 ppm) NO_2 or 1310 $\mu g/m^3$ (0.50 ppm) SO_2. However, following exposures at 0.10 ppm of each gas for 4 hr, injury was noted on all species; at 0.05 ppm of each gas, slight injury was noted on all species except tomato (Tingey et al., 1971a). A greater-than-additive suppression of the apparent photosynthetic rate of alfalfa was obvious when exposed to 660 $\mu g/m^3$ (0.25 ppm) of SO_2 and/or (470 $\mu g/m^3$) NO_2 for 2 hr (White et al., 1974). At 0.15 ppm of each gas singly, there were no measurable effects, but a 7-percent suppression of apparent photosynthetic rates was noted in the mixture (White et al., 1974).

Field exposure of seven different species of plants indigenous to the cold desert areas of the southwestern United States to 1310-28,820 $\mu g/m^3$ (0.50-11.0 ppm) SO_2 singly, or 1310-28,820 $\mu g/m^3$ (0.50-11.0 ppm) SO_2 and 190-9400 $\mu g/m^3$ (0.10-

5.00 ppm) NO_2 combined in 2-hr fumigations resulted in no evidence of more-than-additive foliar injury (Hill et al., 1974).

More-than-additive foliar injury was noted on radish leaves exposed for 1 hr to 1310 μg/m^3 (0.50 ppm) SO_2 and/or 940 μg/m^3 (0.50 ppm) NO_2. No interactive effects were found for other plants tested (oats, Swiss chard, and pea) (Bennett et al., 1975). More-than-additive effects have been associated with the enzyme activity in pea plants exposed to 520 μg/m^3 (0.20 ppm) SO_2 and 190 μg/m^3 (0.10 ppm) NO_2 for 6 days; peroxidase activity was increased and ribulose-1,5 diphosphate carboxylase activity was decreased (Horsman and Wellburn, 1975).

5.2.3 Sulfur Dioxide and Hydrogen Fluoride

Suppression of linear growth and leaf area in the absence of foliar injury of Koethen orange plants exposed to 2100 μg/m^3 (0.80 ppm) SO_2 and/or hydrogen fluoride (2.3-13.0 ppb) for 23 days was no greater-than-additive. Satsuma mandarin plants exposed to the same conditions for 15 days exhibited only additive foliar injury and no growth suppression at all (Matsushima and Brewer, 1972). Greater-than-additive foliar injury was exhibited by barley and sweet corn exposed to 160-210 μg/m^3 (0.06-0.08 ppm) SO_2 and/or 0.60-0.90 ppb hydrogen fluoride for 27 days. Using higher concentrations of SO_2 for only 7 days resulted in simply additive foliar injury. Pinto beans were not injured in any of the treatments (Mandl et al., 1975).

5.2.4 Sulfur Dioxide, Nitrogen Dioxide and Ozone

Fujiwara et al. (1973) combined SO_2, NO_2, and O_3 at concentrations ranging from 0 to 0.2 ppm in an artificially controlled environment and exposed peas and spinach for 5 hr. Ozone was the most injurious, SO_2 was next, and NO_2 elicited only minor injury. More-than-additive foliar injury followed exposure to SO_2 + O_3, but only additive effects were observed with SO_2 + NO_2 or

$NO_2 + O_3$. The addition of NO_2 to the $O_3 + SO_2$ had little effect on foliar injury. Reinert and Gray (1981) examined the effects of 0.2 or 0.4 ppm each of O_3, SO_2, and NO_2 (3- or 6-hr exposures) on the growth of radish. The main effect of each pollutant and the potential interactive effects of each mixture were examined through partitioning. Sulfur dioxide depressed the root/shoot ratio at both 520 and 1050 µg/m^3 (0.2 and 0.4 ppm); however, when NO_2 and SO_2 were both present there was a greater than additive depression of the root/shoot ratio at 1050 µg/m^3 (0.4 ppm).

5.2.5 Sulfur Dioxide and Biotic Plant Pathogen Interactions

Plant disease is caused by the interaction of a plant and a pathogen acting under suitable environmental conditions. The influence of SO_2 directly or indirectly on the interrelationships of a given plant and its possible biotic pathogens has been difficult to investigate. Additionally, whenever the variables of the physical environment are considered within such experimental sequences, the subject becomes even more difficult to examine. Laurence (1978) and Heagle (1973) have provided the most recent reviews of the interaction between air pollutants and plant parasites.

In seven of nine plant diseases reported in SO_2-related studies as reviewed by Laurence (1978), there was either no effect or a reduction in disease development demonstrated. Disease increased only in needle cast of pine (Chiba and Tanaka, 1968), and increased virus titer of southern bean mosaic virus has been reported by Laurence et al. (1981).

In a recent study by Laurence et al. (1979) maize and wheat were exposed to 0.10 or 0.15 ppm SO_2 for either 2 or 10 days and innoculated at various times with Helminthosporium maydis or Puccinia graminis. The ability of these fungi to infect either corn or wheat, respectively, was inhibited by SO_2 exposures; greater inhibition occurred if plants were fumigated prior to inoculation attempts.

Studies done under ambient conditions without monitoring of other pollutants have suggested a decrease in disease incidence in areas of higher SO_2 pollution with the possible exception of those pathogens that are able to better invade weakened plants. If SO_2 exposure has resulted in an overall weakened condition, other agents, such as root-invading fungi, may be able to gain entrance into an otherwise resistant host. Such is the suspected reason for increased incidence and severity of attack by the root pathogen *Armillaria mellea* in trees weakened by SO_2 (Donaubauer, 1968; Kudela and Novakova, 1962; Jancarik, 1961).

The effects of SO_2 on infection by organisms other than fungi have also been studied. *Abies concolor* and *A. vertchi* were severely attacked by plant lice in an environment of high SO_2, but *Pinus strobus* was attacked less and *P. griffithi* and *P. sylvestris* were not attacked (Stewart et al., 1973).

5.2.6 Summary

As can be seen from the preceding analysis of research dealing with pollutant mixtures, plant species vary in their response and the type of response (additive, less-than-additive, greater-than-additive) may depend on the parameter measured. Understanding of how pollutant combinations influence plant growth and development, and how environmental factors can modify those responses is still fragmentary. Insufficient information exists to determine the influence of pollutant sequencing during combination exposures, meteorological influences, the effect of various cultural practices, and many other variables in relation to vegetational effects induced by SO_2 combined with other pollutants.

There is a need to determine the best technique for evaluating the effects of pollutant mixtures. Only recently has the partitioning technique been utilized to elucidate the effects of individual pollutants in pollutant mixtures.

This technique allows for separation of the main effects of each pollutant and also provides a statistical test of the significance of potential interactions between pollutants.

Analysis of the data indicates that interactions can occur between pollutants and, because the occurrence of pollutant mixtures is typical of the ambient atmosphere, knowledge of interactive effects is very important. However, the nature of the effects of pollutant mixtures is extremely complex. Most research studies have necessarily taken a rather simplistic approach to this complex problem. It is, therefore, difficult to relate these relatively few results to "real world" situations.

5.3 EFFECTS OF SULFUR DIOXIDE ON NATURAL ECOSYSTEMS

5.3.1 Sulfur Dioxide In Terrestrial Ecosystems

Sulfur is an element that is essential for the normal growth and development of plants and animals. It is a basic constituent of protein and is required in large amounts by some plants. Under normal circumstances sulfur in rainwater and in soil organic matter is sufficient to meet plant requirements. Excessive sulfur in the form of sulfur dioxide however, can be toxic to plants. The phytotoxic forms of sulfur, routes of entry into plants, and the symptomatology of SO_2 injury to plants have been discussed in the preceding sections.

Within any ecosystem, nutrient sources are to be found in the atmosphere, in living and dead organisms, and in available and unavailable salts in the soil and rocks. The nutrients are cycled from the living to the nonliving components and back again. Air pollution, however, can disrupt nutrient cycling by altering the amounts in the various compartments and the rate of flow among them (Smith, 1980).

There are two types of biogeochemical cycles, the sedimentary and the gaseous. The sulfur cycle includes both. Sulfur enters the atmosphere from the combustion of fossil fuels, from volcanic eruptions, from the surface of oceans and in gases released by decomposition processes. Anaerobic decomposition of organic matter releases hydrogen sulfide (H_2S) into the atmosphere where it is quickly oxidized into sulfur dioxide. Sulfur dioxide is soluble in water and may be carried back to earth in rainwater as dilute sulfuric acid (H_2SO_4) (Smith, 1980). Regardless of the source, sulfur in soluble form is taken up by vegetation and is incorporated through a series of metabolic processes, including photosynthesis, into sulfur-containing amino acids. Sulfur is transferred from the producers to the consumers in food and through excretion and death back to the soil and to the sediments in the bottoms of ponds, lakes, and seas where bacterial action releases it as hydrogen sulfide or as sulfate. Sulfur in the long-term sedimentary phase is tied up in organic and inorganic deposits in the soil, and sulfur is added to ecosystems through geological weathering and meteorological processes, with the latter being the predominant source. Weathering and decomposition permit sulfur to enter into solution and to be carried into aquatic and terrestrial ecosystems. In its gaseous state, sulfur is circulated on a global scale (Figure 2-1).

Based on empirical watershed studies (Shriner and Henderson, 1978; Likens et al., 1977) and modeling (Coughenour, 1978), the soil is a major reservoir for atmospherically derived sulfur within ecosystems. The majority of soil sulfur is unavailable to vegetation and is organically bound in the humus (May and Downes, 1968). Microbial activity oxidizes organically bound sulfur to sulfates. Sulfates may be taken up by plants or leached from the soil. The rate of sulfur released from the organic to the inorganic compartment is the major factor controlling the movement of sulfur between the soil and vegetation (Moss, 1976; May et al., 1972). A distinction between natural and agroecosystems is that soils in agroecosystems through continued cropping are depleted of their supply of organic sulfur, and it is not renewable; therefore, sulfur must be added as fertilizer. Sulfur dioxide brought down in precipitation is also added to the soil. The amount of sulfur added to soils through precipitation will depend on the industrial activity of the surrounding area (Kamprath, 1972).

The influence of anthropogenic sources of sulfur on the sulfur cycle is most pertinent when addressed on a regional basis (Granat et al., 1976) as Shinn and Lynn (1979) have done for the northeastern United States. Comparing global versus regional sulfur cycling, atmospheric sulfur additions are not equally distributed over the global land areas, and the northeastern United States experiences anthropogenic atmospheric additions of sulfur that are 28.4 times that expected if additions were distributed uniformly over the globe. The most notable contrast between the global and regional sulfur cycle is the importance of atmospheric sulfur sources. Globally, natural processes far exceed anthropogenic contributions, whereas in the northeastern United States human activities generate 12.5 times the amount of sulfur released by nature. A total of 27×10^6 tons of SO_4 enters the northeastern regional atmosphere annually and 13×10^6 tons are deposited within this region by wet and dry deposition; the remaining sulfur is exported to other areas of the globe.

Based on the above information, man is clearly a major source of atmospheric sulfur within the United States and, in the Northeast alone, anthropogenic sources exceed all others by a factor of 12.5. Within this region, SO_2 levels annually average 16 $\mu g/m^3$ (0.006 ppm) (Shinn and Lynn, 1979), which is several times that recorded in pristine areas. The immediate fate of approximately 60 percent of this atmospheric sulfur is deposition on terrestrial and aquatic ecosystems; however, the subsequent fate of sulfur within the ecosystem is not fully known. Experimental evidence from forested watersheds coupled with results from simulation models indicates that sulfur in ecosystems is highly mobile. Although sulfur levels in the soil and vegetation compartments in developing and mature forest ecosystems impacted by SO_2 increase with time, the majority of sulfur deposited annually is exported out of the system in stream flow.

The conclusion that SO_2 emitted into the atmosphere through anthropogenic activity is ultimately transferred to terrestrial and aquatic ecosystems is well documented (Meszaro et al., 1978). Unfortunately, the fate of sulfur in the ecosystem after deposition is not fully resolved. The issue is critical since ecosystems subject to excess nutrients or toxic materials do not commonly distribute them uniformly throughout the system but rather preferentially sequester them in specific pools or compartments. In addition, sulfur dioxide as a gas can cause injury to the vegetative components of an ecosystem so that energy flow and the cycling of other nutrients as well as sulfur may be disrupted.

5.3.2 Ecosystem Response to Sulfur Dioxide

Pollutants often reduce community diversity when an ecosystem becomes simplified through the removal of pollutant-sensitive plant species. Woodwell (1970) has described the effects of pollution on the structure and physiology of ecosystems. The studies that follow discuss the ecological changes in a forested ecosystem resulting from sulfur gas emissions.

The Kaybob I and II gas plants (Fox Creek, Alberta, Canada), which emit SO_2 during the removal of hydrogen sulfide from natural gas, are located within the transition Montane-Boreal forest that is dominated by a mixed assemblage of deciduous and coniferous trees; however, white spruce (*Picea glauca*) is predominant in successional stands on well drained soils. (Winner and Bewley, 1978a,b; Winner et al., 1978). Because these white spruce forest have less species variation than other sites, they were selected for analysis along a transect showing decreasing So_2 stress. The Kaybob facility began operation in 1968, and the field study was conducted during the summers of 1975 and 1976. From 1973 to 1975, it is estimated that the Kaybob facility emitted approximately 71,000 kg per day of SO_2 (Winner and Bewley, 1978b).

Relative species diversity showed no gradient pattern of response to SO_2; however, the percent of coverage by all understory plants, including vascular plant species and mosses, showed a marked increase with distance from the source (Winner and Bewley, 1978b). White spruce seedlings close to the refinery were reduced in number. Changes in moss communities were conspicuous and included decreasing values for moss canopy coverage, moss carpet depth, dry weight, and capsule number and for the frequency of physiologically active versus inactive moss plants. Close to the source, there were no mosses at all (Winner and Bewley, 1978a). These results indicate that species diversity, particularly in the mosses, has changed as a consequence of sulfur gas emissions. The changes in diversity observed during the summers of 1975 to 1976 probably were initiated soon after the facility began operation in 1968 and the effects will be observed as long as the facility is operational. Atmospheric SO_2 concentrations were not reported but it is evident that operational upsets, particularly during the early years of plant operation, resulted in high emission rates from the low elevation flare sources causing high SO_2 concentrations near the ground in this area.

In a subsequent study, Winner et al. (1978) used sulfur isotope ratios to determine the fate of sulfur emissions from the natural gas plants. The ^{34}S value of SO_2 emitted from gas refineries is higher than that for nonindustrial sources in the study area. Through the use of this tracer, it was determined that mosses absorb only airborne sulfur, whereas the sulfur in conifer needles is derived from both air and soil. Krouse (1977) in his study of the Ram

River area of Alberta made a similar determination. Winner et al. (1978) conclude that because mosses act as a sink and accumulated large quantities of sulfur, they are more vulnerable than vascular plants to effluents such as SO_2. Further, they state that mosses participate in the process of soil formation, prevent erosion, and play a role in succession. Removal of the moss carpet would ultimately be expected to influence the growth of the vascular plants in the ecosystem because when mosses are not present soils accumulate SO_2 rapidly.

In another, more detailed study of the effects of low-level sulfur dioxide emissions on a forested ecosystem, it was observed that the main ecological process that was directly and indirectly affected by the sulfur gas emissions was nutrient cycling (Legge et al., 1981, Legge 1980). The study concluded that the chronic exposure to sulfur gas emissions over time resulted in an alteration of the mineral nutrient balances of the various ecosystem components and modified the biological relationships among the components. Further, the four-year study begun in 1972, concluded that despite measurable deterioration of the forest ecosystem in the West Whitecourt study area, it did not appear that the sulfur gas emissions caused irreversible ecological degradation, particularly in view of the significant reductions in sulfur gas emissions that have resulted since the inception of the West Whitecourt Gas Plant situated in west central Alberta, Canada (Legge et al., 1981; Legge, 1980).

The region studied by Legge et al. (1981) was being subjected to the effluents from the West Whitecourt "sour gas" processing plant. "Sour gas" is natural gas (methane) that contains hydrogen sulfide (H_2S). For commercial use, the hydrogen sulfide is removed from the methane as elemental sulfur by a chemical process. Any H_2S not converted to elemental sulfur is incinerated in excess air and methane in a high temperature (580°C) furnace and oxidized to

SO_2, which is then vented to the atmosphere from a tall (122 m) incinerator stack. Smaller flare stacks are used to vent the effluents from the burning of small waste quantities of sulfur recovery gas plant process and compressor gases. Except when operational upsets occur within the gas plant, at which time the flare stacks may for short periods of time contribute more gas emissions to the atmosphere daily than the incinerator stack, the incinerator stack is the main source of SO_2 emissions. Since the gas plant began functioning in 1961-62, the SO_2 output has dropped from 600 to 36 metric tons per day in 1976 because of improved operating procedure.

The vegetation of the Whitecourt study area is within the predominantly forested subregion of the Boreal Forest of Canada and is characterized as a transition forest area between the Boreal and Subalpine Forest Regions. The tree populations in the area are hybrid representatives of lodgepole pine x jack pine (*Pinus contorta* Loud. x P. *banksiana* Lamb. and of the alpine fir x balsam fir [*Abies lasiocarpai* (Hook.) Hutt. x *A*. *balsamea* (L.) Mill.]

To determine the effect of low-level sulfur dioxide emissions on the forested ecosystem, and integrated ecological approach was used to study and explain the changes in ecosystem structure and function. The four-year study begun in 1972 divided the ecosystem into four major components (air, vegetation, soil, and water) and developed a conceptual model to illustrate the dynamic relationship between the sulfur dioxide "source" and the generalized ecosystem "sink" (Legge et al., 1981; Legge, 1980).

Five experimental sites were located progressively downwind in the main path of the sulfur dioxide emissions. The two intensive experimental sites were located 1.0 and 1.5 km east of West Whitecourt Gas Plant. Analysis of the ambient air monitoring data from the two intensive sites during the 1975 and 1976 growing seasons revealed that the air quality standard for sulfur dioxide of 0.2 ppm per half hour per 24 hours as set by the Alberta Department of the Environment was exceeded on only three occasions at the two sites in over 2500 hrs of monitoring. Much higher concentrations existed at this sampling site from 1961-74, however, and effects on soil pH, nutrient balance and tree growth would have also been influenced by these higher concentrations. In addition, it was observed that the stable sulfur isotopic composition ($^{32}S/^{34}S$) of the sulfur dioxide emissions from West Whitecourt Gas Plant was different from the natural background sulfur and so provided a tracer that indicated that the gas plant was the major source of the sulfur gas detected in the forest ecosystem (Legge et al., 1981, Legge 1980).

The gas exchange properties of field acclimated lodgepole x jack pine trees were measured to determine the short- and long-term effects of chronic exposure to sulfur gas. Photosynthetic rates and leaf resistance of the trees had been modified. The extent of ecological modification was dependent on the distance from the sulfur source. The rates of photosynthesis were lower and leaf resistance rates were higher nearer the source of sulfur gas. The reduced rate of photosynthesis was only partially attributable to inceased leaf resistance; therefore, ecological factors such as the mineral nutrient status of foilage and soil pH were studied since these parameters were known to modify plant response (Legge et al., 1981).

Analysis of the foliage of the lodgepole x jack pine trees indicated that the sulfate-sulfur concentration decreased with increasing distance from the sulfur gas emission source. The decrease in foliar sulfate concentration was also more pronounced with increased foliar age. In addition, detailed analysis of foliar mineral nutrient concentrations revealed that the mineral nutrient status of the trees had been altered. The concentration of P, K, Fe, Mg, N, and Zn in the foilage tended to increase with distance from the West Whitecourt Gas Plant while the concentration of Ca and Al tended to decrease. Much more than any of the other minerals sampled, the Mn concentration in the foilage tended to decrease as the distance from the sulfur source increased. Reduction in foliar potassium and phosphorus may be associated with reduction in the rate of photosynthesis since foliar potassium has been linked with stomatal activity and phosphorus with phosphorylation. The alteration of mineral nutrients in the foilage of the lodgepole x jack pine trees is, therefore, an important ecological factor contributing to the modification of plant response by sulfur gas emissions (Legge et al., 1981 and Legge, 1980).

Soil pH is known to affect the availability of mineral nutrients to plants, therefore, soil pH profiles were measured. Soil pH and soil carbonate values increased with depth in 100 cm profiles and with distance away from the West Whitecourt Gas Plant. A direct relationship was found between lowered soil pH and the elevated levels of foliar Mn in lodgepole x jack pine trees. This relationship suggests that the foliar Mn concentration could be used as an indicator of mineral nutrient modification of the forest ecosystem by sulfur gas emissions.

Total sulfur in the soil likewise decreased with depth and distance from the sulfur dioxide emission source suggesting that sulfur is tied up in the organic matter and released very slowly. No relationship was found between soil pH and $\delta\ ^{34}S$ values in the soil; however, the soil $\delta\ ^{34}S$ value was found to be an excellent indicator of the presence and penetration into the soil profile of sulfur originating from sulfur gas emissions, while soil pH indicated sulfur loading.

Biochemical changes in the trees were also noted. The most significant was a transient metabolic effect involving adenosine triphosphate (ATP). ATP was found to decrease significantly in the foilage of the trees when they were exposed to low concentrations of SO_2 for a short duration. Foliar ATP concentrations returned to the pre-SO_2 fumigation levels when the fumigation ceased. Trees grown in the laboratory in the absence of sulfur gas emissions showed no fluctuation in foliar ATP concentrations and the ATP concentraton was three times the content of field-grown trees. The lower concentration of ATP in the foilage of field-grown trees when compared to laboratory-grown trees suggests a partial explanation for the lowered photosynthetic capacities of the lodgepole x jack pine trees growing in the Whitecourt area.

The observed ecological modifications of the forest ecosystem, such as reduced needle biomass (premature needle drop), reduced biochemical energy, reduced photosnthetic rates, reduced soil pH, disruption of mineral nutrient cycling, foliar sulfur loading when combined with a shortened growing season, it was assumed, should be measurable as a reduction in forest production. There was a definite reduction in annual basal area increments in the lodgepole x jack pine trees since 1962 that was attributed to sulfur dioxide emissions from the West Whitecourt Gas Plant indicating that ecological modifications were initiated long before the study began in 1972. The maximum reduction in basal area increments occurred nearest the plant and the reduction fell to zero at 9.6 km. The area affected by sulfur gas during the past 14 years is estimated at 454 km^2 (175 mi^2) or 45,373 ha (112,130 acres). The significant reduction in sulfur dioxide emissions since 1970 suggests that the areas being impacted by the sulfur dioxide will decrease in the future, thus permitting the recovery of the portion of the ecosystem no longer exposed to sulfur dioxide stress.

In the near future, the grasslands of the upper plains will be subject to SO_2 emissions from new coal-burning power facilities that are being construced in areas rich in coal reserves (Durran et al., 1979; Preston and Lewis, 1978). To address this problem, plots of Montana grasslands were exposed to SO_2 during growing seasons of successive years. The monthly median exposure levels were approximately 0, 52 $\mu g/m^3$ (0.02), 106 $\mu g/m^3$ (0.04), and 185 $\mu g/m^3$ (0.07 ppm) SO_2 and were delivered by a zonal air pollution system of ZAPS (Lee et al., 1978). Under the ZAPS system, the SO_2 is delivered through a system of pipes supported approximately 75 cm above the soil surface. Though the flow rates through the system are constant, the canopy-level concentrations vary depending upon the meteorological conditions, principally wind speed and temperature, so that concentrations are often higher near the pipes. Field observations over four years verified that these concentrations were not sufficient to elicit any leaf lesions characteristic of acute SO_2 injury (Heitschmidt et al., 1978). Ambient pollutant concentrations were typically greater at night, and the concentration decreased rapidly from the interface of turbulent air and grass canopy downward to the soil (Preston, 1979).

The most prevalent producer species within the grassland is a perennial, Agropyron smithii. In populations sampled over the growing season in each of the exposure regimes, SO_2 induced a variety of changes in biochemical indices of plant performance. Monthly samples of tillers and leaves showed a positive correlation of foliar sulfur with time of exposure and canopy-level SO_2 concentrations (Lauenroth and Heasley 1980). This relationship was most conspicuous with the two higher exposure regimens, and total foliar sulfur in the highest exposure plot was three times greater than that in vegetation sampled from control locations (Laurenroth and Heasley, 1980). As the sulfur content of leaf tissue increased, the ratio of nitrogen to sulfur decreased (Lauenroth and Heasley, 1980).

These biochemical changes in the major producer species were mirrored by other modifications in plant performance. In A. smithii populations exposed to 52 $\mu g/m^3$ (0.02 ppm) SO_2 over the growing season, the functional leaf life (the period of active photosynthesis) was increased by several weeks, while the same index of plant performance was shortened by two weeks at 106 (0.04 ppm) and 186 $\mu g/m^3$ (0.07 ppm) SO_2 (Lauenroth and Heasley, 1980). Parallel increases and decreases in chlorophyll content at the low and high SO_2 levels, respectively, were also recorded, however, the measurements of net primary production from harvested samples over a period of 5 years revealed no significant treatment response. Finally, the single significant crop change noted was a decrease in the carbon stored in the rhizomes of western wheatgrass (Lauenroth and Heasley, 1980).

Dominant producers were not the only flora exhibiting sensitivity to SO_2. In simulated pollutant exposure using a bisulfite solution, Sheridan (1979) showed that nitrogenase activity in a major component of the lichen flora (Dollema tenex) was reduced. Although the applicability of the data must be validated through field studies, the potential for such an effect must be recognized, particularly in the light of the importance of soil lichens in regulating nitrogen fixation in the grasslands (Sheridan, 1979).

Further evidence of SO_2-associated effects on grasslands is recorded in both consumer and decomposer populations. The density of grasshoppers, a major consumer of A. smithii foilage, decreased 25 percent in two successive seasons with increasing SO_2 stress, (Lauenroth and Heasley, 1980).

Decomposition rates were apparently also altered with less litter disappearance in SO_2-exposed plots. The mechanism involves a direct pollutant effect on decomposer activity rather than an indirect effect, such as an increased sulfur concentration in the litter (Lauenroth and Heasley, 1980).

Larger consumers also exhibited responses reflecting the presence of SO_2 in the atmosphere; however, the responses were not dose dependent (Chilgren, 1978). Peromyscus maniculatus, prairie deer mouse, is a common and active vertebrate in grassland communities. Over one exposure season, the frequency of P. maniculatus in control plots increased, implicating an SO_2-induced behavioral response (habitat preference) whereby individuals seek habitats free of the pollutant.

In summary, at SO_2 levels above 52 $\mu g/m^3$ 0.02 ppm), SO_2 induced changes in the performance of producers, consumer, and decomposers. Many of the responses are individually small, but collectively, over time, they are gradually modifying the structure and function of the grasslands. The significance of these changes to the long-term persistence of the ecosystem remains controversial (Preston, 1979). This is particularly true since in the Montana studies plots were not replicated; on the other hand, the fact that the results are based on data accumulated over several years tends to add to its credence.

The results of these studies, particularly the West Whitecourt and Montana grasslands studies, document the usefulness of addressing ecosystem-level responses to SO_2 from a multidisciplinary approach incorporating investigations of physiology, autecology, synecology, geochemistry, meteorology, and modeling. The results confirm that producers are sensitive to direct SO_2 effects as evidenced by SO_2-associated changes in cell biochemistry, physiology, growth, development, survival, fecundity, and community composition. Such responses are not unexpected. An equally important point of agreement among the different research efforts is the potential for ecological modification resulting from either direct SO_2 effects on nonproducer species or direct changes in habitat parameters, which in turn affect an organism's performance. Changes in biogeochemistry, particularly in the soil compartment, are notable responsive to chronic SO_2 exposure.

The influence of prolonged SO_2 exposures on plant communities is not well documented; however, a hypothetical basis is emerging from which to evaluate effects. This conceptual effort is exemplified by the development of a generalized forest growth model (Botkin et al., 1972) that was designed to assess the consequences of the long-term interactions of air pollution stress and forest community dynamics (Shugart and West, 1977; Botkin, 1976). This model has been applied to determine the response of a mixed-species, deciduous forest in the southeastern United States to the different levels of growth reduction (0, 10, and 20 percent) occurring following simulated pollution stress (West et al., 1980). Over several decades, simulated pollution stress altered the biomass importance of the major tree species within the forest; some species populations increased while others decreased in importance. These results suggest that competitive interactions among species may significantly modify both the level and direction of change in growth rate of individual species in response to air pollution stress. Stand age was also shown to influence strongly the role of competition in modifying responses of individual species within the forest community. Since community composition is determined in part by species interactions (e.g., competition, symbiosis), the ecological importance of resistant species, whose prominence in the community is determined by interaction with sensitive species, can be expected to be enhanced under stresses such as air pollution that do not affect all species equally (West et al., 1980). An understanding of the governing role of species interactions is essential for predicting how ecosystems will respond when exposed to low concentrations of pollution (Botkin, 1976). This is also the justification for not extrapolating freely the results from intensely managed forest and agroecosystems to predict how a mixed species community (e.g., natural forests or grasslands) will respond to a comparable perturbation (Kickert and Miller, 1979; Miller and McBride, 1975).

The results from community-level studies in areas experiencing chronic levels of SO_2 lend credence to the modeling effort. Using communities composed of only 2 or 3 different species, Guderian (1967) analyzed community-level responses to SO_2 and their underlying causes. Changes in community composition were a function of pollutant dose; the higher the dose, the more rapidly the community changed. Altered community composition was attributed both to direct SO_2 effects on populations of sensitive species and to indirect changes in species interactions. Community biomass exhibited little quantitative change, but striking differences in species composition. Similar conclusions have been reached in studies of natural plant communities experiencing prolonged SO_2 exposure (Rosenberg et al., 1979; Guderian and Stratmann, 1968). Rosenberg et al. (1979) assessed species composition in 27 stands of a natural regrowth of a Northern hardwood forest dominated by oaks (_Quercus_ _spp_.), white pine (_P_. _strobus_), and hemlock (_Tsuga_ _canadensis_). The stands, which varied in their distance from a 25-year-old coal-consuming power plant, exhibited no obvious _a_ _priori_ compositional differences. Atmospheric pollutant levels were not reported although foliar symptoms typical of SO_2 toxicity were recorded on several occasions. In both upwind and downwind directions, the number of vascular plants (canopy, understory, and ground) per unit area (species richness) increased with distance from the source; however the differences were greater downwind. A similar distance-dependent response was also recorded for species diversity (Shannon-Weiner). For both species richness and species diversity, the rates of increase were more gradual downwind from the power plant. In spite of these SO_2-induced changes in community composition, an index of aboveground biomass (basal area of overstory species) exhibited no variation among stands. Among the vascular plants, shrub and ground vegetation was more sensitive (diversity and richness) than the overstory to SO_2 stress. This susceptibility of the lower strata was attributed to the intense competition among individuals at an early phase in their life history when they are more sensitive, and to microhabitat factors that tend to increase SO_2 levels close to the ground.

Some of the most notable examples of SO_2 affecting plant communities are the responses of cryptogamic flora (lichens and mosses), and several reviews are available (Hawksworth, 1971; DeSloover and LeBlanc, 1968). In general, the higher ambient SO_2 levels were consistently associated with fewer species and an increasing relative frequency of crustose versus foliose or fruticose forms. The fidelity with which community composition changes in accordance with SO_2 has led to the suggestion that analyses of lichen communities be used as a bioassay to estimate ambient SO_2 levels.

Similar mapping efforts are reported for several regions of North America. In a rural area of Ohio surrounding a coal-consuming power station (emitting 929.88 metric tons SO_2 per day), the distribution of two corticose lichens, *Parmelia caperata* and *P. ruderta*, was markedly affected by high SO_2 concentrations (Showman, 1975). In regions experiencing an annual SO_2 average exceeding 50 $\mu g/m^3$ (0.020 ppm), both species were absent. The distribution of more resistant lichens was not noticeably affected until SO_2 levels exceeded 65 $\mu g/m^3$ (0.025 ppm) (annual average). Somewhat lower levels were projected by LeBlanc and Rao (1975, 1973) to affect the ability of sensitive lichen species to survive and reproduce. Acute and chronic symptoms of SO_2 toxicity in epiphytic lichens occurred when long term (May-October) average concentrations exceeded 80 μg/m^3 (0.03 ppm) and were between 16-80 μg/m^3 (0.006-0.03 ppm), respectively.

The susceptibility of lichens cryptogamic flora to elevated levels of SO^2 may influence the movement of materials within the ecosystem. In the northwestern coniferous forests, lichens fix 2-11 kg/ha of nitrogen, which represents 5-20 percent of the total nitrogen requirement for the dominant producer, Douglas fir (Denison, 1973).

Because the functioning of all ecosystems is due to a network of biotic and abiotic interactions, it may be hypothesized that the effects of SO_2 on producers must have repercussions at other trophic levels. Demonstration of such responses, however, is difficult experimentally, and an accurate assessment of the specific importance of SO_2 in eliciting these responses is complicated by the often complex relationships among producers, consumers, and decomposers.

Consumers and decomposers may respond to SO_2 via a direct, adverse effect of the pollutant. The presence of elevated atmospheric levels of SO_2 is particularly relevant to soil organisms (Babich and Stotzky, 1974). This focus on soil-borne organisms takes on relevance since the rhizosphere is not only biologically active but also the major site for sulfur accumulation within the ecosystem (Legge et al., 1976). In a forested area experiencing atmospheric SO_2 levels averaging 126 μg/m^3 (0.048 ppm), the species composition of soil microflora shifted toward a greater number and frequency of species capable of utilizing the soil sulfur additions (Wainwright, 1979). Specically, the levels of thiobacilli and sulfur-oxidizing fungi were postively correlated with levels of SO_2 stress and soil depth.

The edaphic and climatic environment strongly influences the community of plants, animals and microorganisms that develop at a given site. In natural ecosystems in sulfur deficient soils, communities have evolved with the constraints imposed by a limited supply of sulfur. Although atmospherically derived sulfur may not be sufficient to cause injury, the prolonged input of sulfur may relax the constraints of a limited sulfur supply, thereby inducing shifts in species composition.

5.4 SUMMARY

Sulfur dioxide and particulate sulfate are the main forms of sulfur in the atmosphere. Of the two, sulfur dioxide is potentially more injurious, particularly when it is in combination with other airborne pollutants. Plants may be exposed to these pollutants in several different ways. Dry and wet deposition of gases and particles may bring sulfur compounds into contact with plant surfaces and/or the soil substrate as well. The effects of such external exposures on plants are more difficult to assess than those associated with the entry of SO_2 through the stomata. Plant response to pollutant uptake may be influenced by such dynamic physical factors as light, leaf surface moisture, relative humidity and soil moisture. Such factors influence internal physiological conditions in plants as well as stomatal opening and closing and, therefore, play a major role in determining the sensitivities of the plant species or cultivars.

Sulfur dioxide must enter a plant through leaf openings called stomata to cause injury. Sulfur dioxide, after entering plant cells through the stomata, is converted to sulfite and bisulfite, which may then be oxidized to sulfate. Sulfate is about one-thirtieth as toxic as sulfite and bisulfite. As long as the absorption rate of SO_2 in plants does not exceed the rate of conversion to sulfate, the only effects of exposure may be changes in opening or closing of stomata or insignificant changes in the biochemical or physiological systems. Such effects may abate if SO_2 concentrations are reduced. Both negative and positive influences on crop productivity have been noted following low-dose exposures.

Symptoms of SO_2-induced injury in higher plants may be quite variable since response is governed by pollutant dose (concentration x duration of exposure), conditions of the exposure (e.g., day vs night, peak vs long-term), physiological status of the plant, phenological stage of plant growth, environmental influences on the pollutant-plant interaction, and the environmental influences on the metabolic status of the plant itself.

There are several possible plant responses to SO_2 and related sulfur compounds: (1) fertilizer effects appearing as increased growth and yields; (2) no detectable responses; (3) injury manifested as growth and yield reductions without visible symptom expressions on the foliage or with very mild foliar symptoms that would be difficult to perceive as air pollution induced without the presence of a control set of plants grown in pollution-free conditions; (4) injury exhibited as chronic or acute symptoms on foliage with or without associated reduction in growth and yeild; and (5) death of plants and plant communities.

A number of species of plants are sensitive to low concentrations of SO_2. Some of these plants may serve as bioindicators in the vicinity of major sources of SO_2. Even these sensitive species may be asymptomatic, however, depending on the environmental conditions before, during, and after SO_2 exposure. Various species of lichens appear to be among the most sensitive plants.

As the dose of SO_2 increases, plants may develop more predictable and more obvious visible symptoms. Foliar symptoms progress from chlorosis, or other types of pigmentation changes, to necrotic areas, and the extent of necrosis increases with exposure. Studies of the effects of SO_2 on growth and yield have demonstrated a reduction in the dry weight of foliage, shoots, roots, and seeds, as well as a reduction in the number of seeds. At still higher doses, there are further reductions in growth and yield. Extensive mortality has been noted in forests continuously exposed to SO_2 for many years.

The amount of sulfur accumulated from the atmosphere by leaf tissues is influence by the amount of sulfur in the soil relative to the sulfur requirement of the plant. After low-dose exposure to SO_2, plants grown in sulfur-deficient soils have exhibited increased productivity. Plant growth and development represents an integration of cellular and biochemical process. The response of a given species or variety of plants to a specific air pollutant cannot be predetermined on the basis of the known response of related plants to the same pollutant. Neither can the response be predetermined by a given response of a plant to similar doses of different pollutants.

Each plant is a different individual genetically, and therefore its genetic susceptability and the influence of the environment at the time of exposure must be considered for each plant and each pollutant. The data presented in this chapter exemplify the fact that each plant is a separate entity, and, because of the variation in response shown by the different plant species and different cultivars of the same species, making generalizations is difficult. With this in mind, this chapter concludes that in arid regions, some species of vegetation would probably not show visible signs of SO_2 injury even at concentrations as high as 11 ppm for 2 hours. On the other hand, in many nonarid regions where environmental conditions such as high temperature, high humidity, and abundant sunlight enhance plant responsiveness to SO_2 exposure, many species of sensitive and intermediately responsive vegetation would likely, from time to time, show visible injury when exposed to peak (5 minutes), 1-hour, and 3-hour SO_2 concentrations in the range of 2620-5240 $\mu g/m^3$ (1-2 ppm), 1310-5240 $\mu g/m^3$ (0.5-2 ppm), and 790-2100 $\mu g/m^3$ (0.3-0.8 ppm) respectively.

In general, the studies cited in this chapter indicate that regardless of the type of exposure and the plant species or variety, there is a critical SO_2 concentration and a critical time period after which plant injury will occur. This plant response appears to be associated with the capability of a plant to transform within the leaf toxic $SO_2^=$ and $SO_3^=$ into the much less toxic $SO_4^=$ and ultimately to transfer or break down $SO_4^=$.

At present, data concerning the interactions of SO_2 with other pollutants indicates that, on a regional scale, SO_2 occurs at least intermittently at concentrations high enough to produce significant interactions with other pollutants, principally O_3. A major weakness in the approach to pollutant interactions, however, is the lack of in-depth analysis of existing regional air quality data sets for the three principal pollutants (SO_2, O_3, and NO_2). These data should determine how frequently and at what concentrations the pollutants occur together both spatially and temporally within regions of major concern. The relative significance of simultaneous versus sequential occurrence of these pollutants to effects on vegetation is also not well documented and is critical in evaluating the likelihood and extent of potential pollutant interactions under field conditions.

Natural ecosystems are integral to the maintenance of the biosphere, and disturbances of stable ecosystems may have long-range effects which are difficult to predict. Within the United States, anthropogenic contributions to atmospheric sulfur exceed natural sources. In the Northeast these contributions exceed natural sources by a factor of 12.5, and approximately 60 percent of the anthropogenic emissions into the atmosphere are deposited (wet and dry deposition) on terrestrial and aquatic ecosystems. The subsequent fate and distribution of sulfur in these systems is not well understood. Wet deposition of sulfur compounds will be discussed in a later chapter.

Data relating ecosystem responses to specific doses of SO_2 and other pollutants are difficult to obtain and interpret because of the generally longer periods of time over which these responses occur and because of the many biotic and abiotic factors that modify them.

Vegetation within terrestrial ecosystems is sensitive to SO_2 toxicity, as evidenced by changes in physiology, growth, development, survival, reproductive potential and community composition. Indirect effects may occur as a result of habitat modification through influences on litter decomposition and nutrient cycling or through altered community structure. At the community level chronic exposure to SO_2, particularly in combination with other pollutants such as O_3, may cause shifts in community composition as evidenced by elimination of individuals or populations sensitive to the pollutant. Differential effects on individual species within a community can occur through direct effects on sensitive species and through alteration of the relative competitive potential of species within the plant community.

6. EFFECTS OF PARTICULATE MATTER ON TERRESTRIAL ECOSYSTEMS

6.1 INTRODUCTION

Particulate matter originating from both natural and anthropogenic emission sources is a common component of the atmosphere. The heterogeneous physical and chemical nature of particulate matter presents problems in addressing the significance of elevated atmospheric particulate levels for natural and agroecosystems.

Wet and dry deposition are the two processes by which particles are transferred from the atmosphere to terrestrial ecosystems. The fate of particles deposited on foliar surfaces depends on the solubility of the constituents (chemicals and elements), the occurrence of precipitation, and the sorptive capacity of the leaf (Little, 1973). Furthermore, many elements commonly associated with particles are essential for plant metabolism (e.g., zinc and phosphorus), and as a consequence, absorption may be a means by which the plant can supplement its nutrient supply (Kloke, 1974). Leaf surfaces may be only a transitory site for particulate matter and its associated constituents. If not retained by the leaf, material is ultimately transferred to the forest floor through washoff in rain events. The net effect of these processes is to funnel leaf surface deposits to the litter-soil complex. This conclusion is verified for many atmospherically derived heavy metals deposited in natural ecosystems (e.g., Coughtrey et al., 1979; Thompson et al., 1979).

6.2 PLANT EXPOSURE TO PARTICULATE MATTER

6.2.1 Deposition Rates

Deposition of particles is strongly dependent on particle size. Most sulfates and nitrates are found in the size range of 0.1 to 1.0 μm, and very little information is available on the deposition rate for these particles. Shinn

(1978) divided particulate deposition into three categories based on particle size:

CATEGORY 1.	Particles more than 10 μm in diameter; includes dust and spores.
CATEGORY 2.	Particles between 1 μm and 10 μm in diameter where the sampling efficiency is highly dependent on the particle diameter.
CATEGORY 3.	Submicron particles between 0.1 and 1.0 μm in diameter, which have a nearly constant sampling efficiency.

Current experimental data suggest that sampling efficiencies in Category 3 are less than one-tenth of those in Category 2 (Shinn, 1978). According to Clough (1975), in the range of wind speeds normally encountered, the larger particles in the atmosphere are much more efficiently sampled than the smaller fraction.

Little (1977) evaluated the effects of leaf surface texture on the deposition of monodisperse polystyrene aerosols on the leaf surfaces. Rough and hairy leaf discs collected 5.0 μm particles up to seven times more efficiently than did smooth leaves. Very large differences in particle deposition velocities were observed between the laminas, petioles, and stems of each species. The velocity of deposition of particles to plant surfaces varies according to both wind speed and particle size.

6.2.2 Routes and Methods of Entry Into Plants

6.2.2.1 Direct Entry Through Foliage--Foliage is continuously subjected to natural and man-made coarse particles that are insoluble or sparingly soluble in water. Coarse particles in general are too large to enter leaves through stomata. Based upon a review by Meidner and Mansfield (1968) that presented stomatal data for 27 species of plants (e.g., pine, oak, corn, soybean, and tobacco) the overall average pore (opening) width was 6 micrometers and accounted for 0.15 to 2.0 percent of the total average stomatal area. In certain cases, such as with cement kiln dusts (Lerman and Darley, 1975) and other types of aggregate particles (Smith, 1973), a limited amount of stomatal clogging can occur. This is apparently dependent on the statistical probability of the particulate matter falling on the stomata, the size of the particle, and the stomatal aperture. In many plants, the stomatal opening is on the lower surface. Cement kiln dust forms a crust on leaves, twigs, and flowers. According to Czaja (1961), crusts of this type form because some portion of the settling dust consists of calcium aluminosilicates typical of the clinker from which cement is made. Hydration of the dust on the leaf surface results in the formation of a gelatinous calcium aluminosilicate hydrate, which later crystallizes and solidifies to a hard crust.

When coarse particles are water soluble or have some water-soluble components, plant uptake of ions from the leaf surface does occur. Because of analytical difficulties, the exact magnitude of the uptake is difficult to measure. Since it is not possible to predict the efficiency of any washing procedure used to remove particles from the leaf surface, it is difficult to delineate and separate the concentration of a given element on the leaf surface from its concentration inside the tissue. In addition, leaching of elements from within the tissue is known to occur during the washing (Little, 1973).

Smith (1973) evaluated metal contamination of urban woody plants by using a variety of washing procedures. Indirect evidence from all these studies suggests that a variable concentration of metals originating from coarse particles can accumulate in plant foliar tissue through direct uptake.

At this time, one of the significant problems in deriving conclusions concerning the magnitude of direct foliar deposition and uptake of atmospheric particulates is the lack of coordinated data on size and frequency distribution of the particles and their chemistry, rates of deposition, and dose in conjunction with changes in tissue concentrations over time relative to background conditions.

6.2.2.2 Indirect Entry Through Roots--Many of the inorganic constituents of particulate air pollutants occur naturally in the soil; others of equal or greater importance do not. Deposition of these pollutants may increase the soil concentrations of the chemical species in question. Some of the chronic effects caused by particulate air pollutants may result from changes in soil physics and chemistry and from increased plant uptake of either the added elements associated with the particles themselves or some other soil-borne elements made more available by the influence of the deposited particles (Guderian, 1980).

It should be recognized that only a portion of the total elemental content of the soil is available at a given time for plant absorption (Brady, 1974). As uptake of elements proceeds, there may be a redistribution of nutrients or toxicants in the soil.

The availability of nutrients or other chemical elements from the soil is strongly influenced by type, chemical composition, and acidity of the soils. Plant nutrients, when present in optimal amounts, are usually available at a neutral pH; however, when the soil becomes acidic, toxic elements such as aluminum become available.

6.3 REACTION OF PLANTS TO PARTICULATE EXPOSURE, AGROECOSYSTEMS

Particle-induced injury to plants has most often been associated with sustained accumulation of particles such as dust or fly ash. Few investigations have dealt with direct or indirect chemical interactions at the plant surface or subsequent effects. The toxicity of accumulated heavy metals in soils has been established for several plant species.

The various forms of particles and their associated impacts on plants have been reviewed (U.S. Environmental Protection Agency, 1977; Lerman and Darley, 1975; U.S. Department of Health, Education, and Welfare, 1969). Krupa et al. (1976) and Linzon (1973) have also prepared extensive reviews of heavy metal deposition and impact. Tolerance of plants for heavy metals and fine particles and their bioenvironmental impacts have also been reviewed (U.S. Environmental Protection Agency, 1975).

6.3.1 Dusts

Dust directly affects plants by coating exposed plant parts, including leaves, stems, flowers, and fruits (Linzon, 1973; Katz, 1967; Jennings, 1934). Depending on the chemical nature of the particles and environmental conditions, deposits may accumulate as dry dusts, as encrustations in the presence of free moisture, or as greasy films or tars. Encrustations of particles on leaves result in reduced gas exchange, increased temperature, reduced photosynthesis, and eventual yellowing and tissue desiccation (Daessler et al., 1972; Parish, 1910).

Terminal growth reduction and chlorosis of 2-year needles of hemlocks coated with heavy dust deposits has been reported. Manning (1971) also reported that fungal propagules increased, but bacterial numbers decreased on such needles. Brandt and Rhoades (1972) reported long-term changes in plant community structure and species composition, and later indicated that radial growth rates were reduced in the tree species involved (Brandt and Rhoades, 1973). On the exposed site they demonstrated a reduction in radial growth of red maple (18 percent), chestnut oak (29 percent), and red oak (23 percent) but a 76-percent increase in radial growth of tulip poplars as compared with representatives of these species growing on a similar but nonexposed site.

Reduction in growth of the dominant species (oak, maple) probably gave a competitive advantage to tulip poplar and a greater than expected increase may have occurred.

The deposition of limestone dusts has caused substrate pH changes followed by lichen community changes, namely, replacement of acid-tolerant communities of lichens by more alkaline- tolerant species (Gilbert, 1976). A reversal of this trend occurred in areas where SO_2 was of importance prior to limestone dust emission. No exact pollutant dose of either limestone dusts or SO_2 were reported. Winter SO_2 levels were estimated to average 65 $\mu g/m^3$.

Cement kiln dusts have been collected from precipitators applied to vegetation. Visible effects were demonstrated on beans following application of particles of > 10 µm at rates 0.05 $mg/cm^2/day$ to 0.38 $m^2/cm^2/day$ for 2-3 days. The lower dose induced a slight reduction in carbon dioxide exchange, and the two higher doses reduced carbon dioxide uptake by 16-32 percent (Darley, 1966).

The accumulation of dust caused increased reflection of solar radiation at wavelengths of 400 to 760 nm and has been demonstrated to reduce photosynthesis (Ricks and Williams, 1974). Conversely, increased absorption of solar radiation by dusted leaves at wavelengths 750-1350 nm has been demonstrated to lead to heat stresses within the leaf tissues (Spinka, 1971).

Growth and yield effects induced by the accumulation of dust have recently been reviewed (U.S. Environmental Protection Agency, 1977). Conflicting reports of yield increases and decreases from such accumulation appear to be caused by variations in doses applied, substrate nutrient balances and pH, and other specific physiological interferences with processes such as pollination of fruit trees (Anderson, 1914).

Dusts, therefore, have only been considered of importance to vegetation growing near emission sources. Accumulation of dusts has been demonstrated to reduce photosynthesis and radial-increment growth of some forest tree species but has increased them in other species.

The phytotoxicity of heavy metals, arsenic, and boron has been demonstrated after accumulations in soils and subsequent uptake by various plants. Table 8-7 presents a summation of toxic effects of individual elements (Krupa et al., 1976). Published reports of direct effects on plants from specific sources are discussed in the following paragraphs.

6.3.2 Arsenic

Only one study was available to show foliar uptake of airborne arsenic (Linzon, 1977). Phytotoxicological studies in the vicinity of gold smelters in Ontario, Canada revealed the occurrence of several injuries to vegetation (primarily fireweed, Epilobium angustifolium) as induced by airborne arsenic compounds in a sulphurous plume. Chemical tissue analysis of affected leaves revealed arsenic at 200 ppm as compared to 1 ppm arsenic in leaves collected 50 miles from the source area. Linzon (1977) suggested 10 points of evidence leading to the conclusion of the airborne nature of the toxicant including elevated concentrations on sides of plants closer to the source and correlation of arsenic emissions with corresponding changes in tissue concentrations on an annual basis.

Arsenic sprays have been applied to the foliage of many plants to hasten fruit maturation by causing premature defoliation and chemical changes in the fruit. For example, lead arsenate sprayed on grapefruit trees caused a "fruit gumming" reminiscent of boron deficiency (Liebig, 1966). Boertitz et al. (1976) reported that arsenic deposited at 22 mg/kg on soil reduced the yield of wheat, rye, winter rape, and red clover by 25, 8, 0, and 6 percent, respectively.

6.3.3 Cadmium

Most biologically active cadmium enters plants through root uptake (Jordan, 1975). Small oxide particles (0.01 to 0.03 μm) may enter leaves through stomata, but it is thought that the oxides remain largely inert. Cadmium accumulated by apple leaves may be translocated and incorporated into fruit as they develop (Yopp et al., 1974).

6.3.4 Copper

Wu and Bradshaw (1972) demonstrated that individual plants of *Agrostis stolonifera* growing near metal smelters were selected for by the copper in the soil, thus indicating an indirect effect of within-species simplification within a population through selection.

6.3.5 Lead

Davis and Barnes (1973) reported reduced growth of loblolly pine and red maple seedlings in pots of two forest soils treated with 2×10^{-4} to 2×10^{-3}-molar lead chloride. Lead toxicity symptoms may include fewer and smaller leaves, reduced plant size, leaf yellowing, and necrosis of elder, sugar beet, squash, and bush bean (Schoenbeck, 1973). Plants growing in soil already high in these metals tended to be more sensitive to the addition of metals by air pollution.

6.3.6 Nickel

Plants can absorb and translocate airborne nickel salts (NAS, 1975). Once inside the plant, nickel affects photosynthesis and other processes such as stomatal function (Bazzaz and Govindjee, 1974). In cases of incipient nickel toxicity to vegetation, no definite symptoms have been observed other than growth repression. In cases of moderate or acute nickel toxicity, the chlorosis-like symptoms of iron deficiency are commonly found (Anderson et al., 1973).

6.3.7 Classification of Plant Sensitivity--Heavy Metal Particles

Coarse particles have not been shown to elicit responses in plants in such a manner as to allow plants to be placed into sensitivity classes similar to those developed for gaseous pollutants. Accumulations of particulate matter, such as roadside dusts, cement, quarry particle emissions, or other forms of deposits, such as fly ash, are deposited on all surfaces and induce responses discussed previously. However, heavy metals do elicit different responses in plants, and therefore it is possible to develop lists of particularly sensitive plants.

Heavy metals are constituents of many coarse particles emitted from various sources. To our knowledge, there has not been an organized effort to establish the toxicity of specific chemical constituents of particles in relation to sensitivity groups of vegetation under field conditions. Table 6-1 lists plants that may be sensitive to heavy metals following deposition and various symptoms as expressed following their respective accumulations.

6.3.8 Dose-Response Relationships--Particles

Review of the published literature suggests that it is not possible at present to define, even crudely, dose-response relationships for the effects of particulate air pollutants on plants. Many reports deal only with gross visible effects or tissue accumulation of one or more constituents of the atmospheric particulate matter present. The emphasis of research has been on settleable coarse particles. Since these are conglomerates of several pollutants, their chemical compositions are frequently ill defined, although their sources have often been identified. Little information could be found on the effects of fine particles on vegetation.

Where cause-and-effect relationships have been suggested, generally no information is presented on the actual concentration, particle size, and frequency distributions. Deposition rates and plant effects vary significantly

TABLE 6-1. PLANTS SENSITIVE TO HEAVY METALS, ARSENIC, AND BORON AS ACCUMULATED IN SOILS AND TYPICAL SYMPTOMS EXPRESSED

Metal	Plant	Symptoms	Reference
Arsenic	Snap bean, lima bean, onion, pea, cucumber, alfalfa, legumes, sweet corn, strawberry (on light and sandy soils).	Reduced germination of seeds, rotting of roots, leaf wilt, brown to red coloration of leaves, reduced yield in fruit trees, death.	Liebig (1966) Linzon (1977)
Boron	Barley, var. Atlas 46; lima bean, var. Henderson; kidney bean, var. Navel; oats, var. Riverside; onion, var. Cabot; pea, var. Alaska; peach, var. J.H. Hale; persimmon, var. Kaki; rose, var. Snow White; soybean, var. Wilson, var O'Tootan; wheat, var. Opal; yellow zinnia.	Yellowing of leaf tips, necrosis between lateral veins and midrib of monocotyledons, marginal leaf scorch, downward cupping of leaves, reduced flowering, fruit lesions.	Bradford (1966) Krupa and Kohut (1976) Yopp et al. (1974)
Cadmium	Red oak, birch, trembling aspen, beet, carrot, celery, green pepper, lettuce, radish, soybean, Swiss chard, tomato, winter wheat.	Reduced root elongation, general growth retardation.	Yopp et al. (1974) Jordan (1975)
Copper	Bean, citrus fruits, corn, mustard.	Stunted root development, chlorotic leaves, reduced vegetative growth.	Reuther and Labanauskas (1966)
Lead	Bean dwarf French, var. Carters; beet, corn, fescue, lettuce, lupine, loblolly pine, red maple.	Stunted root growth, shoot retardation, increased leaf abscission, reduced yields.	Yopp et al. (1974)
Magnesium	Orange (only case known from published literature).	Leaf rolling, spiraling inhibition of leaf emergence. • Narrow leaf development.	Embleton (1966)
Manganese	Alfalfa, broadbean, cabbage, cauliflower, cereals, citrus, clover, lespedeza, pineapple, potato, tobacco, tung, barley, var. Atlas 46, var. Herta; yellow birch, cranberry, peanut, potato, var. Kesweck; alfalfa, apple, apricot, barley, bean, brussels sprout, carrot, clover, cotton, lettuce, medic, orange, pea, potato, sugar beet, vetch, wheat.	Necrotic spots on leaves, necrosis of internal bark,marginal leaf yellowing, incurling of leaf margins.	Yopp et al. (1974) Labanauskas (1966) NAS (1973)
Mercury	Broadbean, oxalis, sunflower, bean, butterfly weed, cinquefoil, fern, *Hydrangea*, *Mimosa*, *Oxalis*, privet, sunflower, willow.	Possible reduced growth.	Yopp et al. (1974) Lagerwerff,(1972) Jacobson and Hill (1970)

TABLE 6-1. (continued)

Metal	Plant	Symptoms	Reference
Nickel	Citrus fruit, alfalfa, oats, var. Victory; pear.	Repression of vegetative growth, leaf chlorosis, white or light yellow and green striping.	Vanselow (1966) Yopp et al. (1974)
Potassium	Orange, tung (only case known for published literature).	Fruit coarseness and leaf necrosis, leaves curl downward, marginal leaf necrosis, intervenal chlorosis, plant dieback.	Ulrich and Ohki (1966)
Zinc	Oats, orange, tung, barley, var. Trail; corn, var. Whatley's Prolific, var. Ida Hybrid 330; cowpea, var. Suwannee; wheat, var. Gaines; barley, citrus, oats, sugarbeet.	Uniform chlorosis, reduced terminal growth, twig dieback, chlorotic striping of leaves, stems stiff and erect.	Chapman (1966) Yopp et al. (1974)

Source: Adapted from Krupa et al. (1976)

with particle size. Few studies are available where two independent scientists have evaluated the effects of particles on vegetation with closely comparable physical and chemical properties under reproducible conditions.

Much of the literature refers to particles from point and line sources and their accumulation in or on soils and vegetation. Tissue accumulation of a given element must be considered as a plant response. Soil scientists have contributed most of the information on plant toxicity symptoms that has been obtained under laboratory conditions. Since many of the plant effects observed are due to the accumulation of elements up to toxic concentrations, tissue concentrations prior to actual exposure will affect the amount and elemental composition of particles that plants can tolerate. Dose-response relationships are therefore determined and predetermined by the background concentrations of various elements in the soil where the plant is growing.

Effects of surface accumulation of cement kiln dust on bean leaves have been investigated by Darley (1966). Doses of 0.6-3.8 g/m per day were applied for 2 or 3 days, and foliar injury and reductions in carbon dioxide exchange were observed. Reductions in carbon dioxide exchange of up to 33 percent were noted in the absence of visible foliar injury. Bean leaves dusted with cement kiln dust at the rate of 4.7 g/m^2 per day for 2 days and then exposed to dew developed leaf rolling and intervenal necrosis (Lerman and Darley, 1975). Leaves not exposed to dew following the dust treatment remained asymptomatic.

Reduced yields and injury to leaves and flowers of several plant species were observed when the plants were exposed once a week for 4 weeks to a dust containing cadmium, lead, copper, and manganese (Krause and Kaiser, 1977). Yield reductions of up to 36 percent were noted.

Plants accumulate different elements at differing rates. Tissue concentrations of some elements are known to be significantly higher in the vicinity of a source for those elements in comparison with background or

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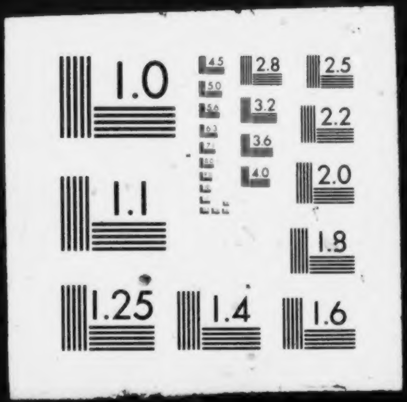


baseline concentrations. This elevated tissue concentration may be due to direct foliar uptake or uptake from the pollutant accumulations in the soil. In many cases, elevated tissue concentrations of a given metal or metalloid are not paralleled by visible injury.

Demonstration of injury symptoms on vegetation under field conditions as a result of accumulation of metals or metalloids is rare. The demonstrated cases are for strip mine wastes. Predicted effects from atmospheric deposition include plant community changes, chronic long-term physiological changes, and indirect effects through a modification of the response to other types of stress. Thus, the state of our knowledge concerning the effects of particles on vegetation is inadequate at this time and does not allow the development of accurate dose-response curves.

6.4 INTERACTIVE EFFECTS ON PLANTS WITH THE ENVIRONMENT--PARTICLES

Few studies have examined the influence of dusts or heavy metal containing particles on the interactions between organisms capable of causing disease and the predisposition of the host plant to the disease process.

Infection due to the fungus *Cercospora* sp. increased on sugar beet leaves exposed to cement dust of 36 percent calcium oxide and 15 percent silica (Schoenbeck, 1960). Increased occurrence of fungus-induced leaf spots on wild grape and sassafras has been observed near a source of heavy emissions of limestone dust (Manning, 1971). After examining 40 leaves in each of five locations exposed and not exposed to the dust accumulations, he found that disease development was two to three and six to seven times greater, respectively, for the two leaf spot fungi in the exposed areas.

Natural exposure to combustion nuclei from automobile exhaust, which supplied increased levels of Aitken nuclei and atmospheric lead, reduced germination of uredospores of *Puccinia striiformis* (stripe rust of wheat); *in* situ development of disease was prolonged about 4 days. Similar studies at an unexposed site did not result in decreased spore germination (Sharp, 1972, 1967).

6.5 RESPONSE OF NATURAL ECOSYSTEMS TO PARTICULATE MATTER

Given the regional character of particulate emissions, particularly along the east coast (U.S. Environmental Protection Agency, National Air Quality, Monitoring and Emissions Trends Report, 1978b), the fate of particulate matter in terrestrial ecosystems experiencing low levels of particulate pollution needs to be assessed. In a deciduous forest in the Southeast, wet and dry deposition of aerosols, gases, precipitation and large particles were major sources of trace element input to the forest floor, including 99 percent for lead, 44 percent for zinc, 42 percent for cadmium, 39 percent for sulfate and 14 percent for manganese (Lindberg et al., 1979). These seemingly large percentages are typical for rural or remote areas even though three major coal consuming power facilities (total coal consumption of 8 x 10^6 metric tons per year) were within 20 km of the forest studied.

Irrespective of the source of particles deposited in the forest, the atmosphere contributed a major portion of the trace element inputs (Lindberg et al., 1979). Water solubility was critical since insoluble constitutents associated with the particulate matter were not readily mobilized within the forest. Any event promoting solubilization (e.g., aerosol formation, rainfall scavenging, moisture formation on leaves) enhanced an element's mobility.

The leaf surface is not the only accumulation site for particles and their associated constituents within the ecosystem. Through precipitation scavenging of particles in air, washoff of surface deposits, or litterfall, particles are transferred to the soil where they are tightly bound to decaying organic matter. The upper soil horizon, including the decaying organic material, is a region of intense biological activity as a result of the physical degradation of litter, remineralization of the bound materials and root uptake of the plant-available nutrients. Consequently, particulate emissions that interfere with microbial activity can have delayed effects on primary production (Tyler, 1972) and soil consumer species.

In summary, even though the impact of particulate matter on terrestrial ecosystems is most apparent near large emission sources, ecosystems within the same geographic region may be the site of deposition. Foliar surfaces are the most common site for initial dry and wet deposition; however, most material is eventually transferred to the soil. Particulate matter alone constitutes an ecological problem only where deposition rates are high. However, concern for terrestrial ecosystems must also address elements and chemicals that may be associated with the particulate matter. Solubility of these particulate constituents is a critical factor since insolubility limits mobility within the ecosystem. One common behavior of particles is their tendency to accumulate selectively within a given component of the landscape. Soils are long-term sites for the retention of many constituents found in particles. While this accumulation in the soil-litter layer has had demonstrable adverse consequences for ecological processes such as decomposition, mineralization, nutrient cycling and primary production around some point sources, the much lower levels chronically deposited over large regions have not yet produced documented adverse impacts on natural ecosystems.

6.6 SUMMARY

A few studies have reported that combinations of particulate matter and SO_2, or particulate matter and other pollutants, increase foliar uptake of SO_2, increase foliar injury of vegetation by heavy metals, and reduce growth and yield. Because of the complex nature of particulate pollutants, conventional methods for assessing pollutant injury to vegetation, such as dose-response relationships, are poorly developed. Studies have generally reported vegetational responses relative to a given source and the physical size or chemical composition of the particles. For the most part, studies have not focused on effects associated with specific ambient concentrations. Coarse particles such as dust directly deposited on the leaf surfaces can result in reduced gas exchange, increased leaf surface temperature, reduced photosynthesis, chlorosis, reduced growth, and leaf necrosis. Heavy metals deposited on the leaf surfaces can result in reduced gas exchange, increased leaf surface temperature, reduced photosynthesis, chlorisis, reduced growth, and leaf necrosis. Heavy metals deposited either on leaf surfaces or on the soil and subsequently taken up by the plant can result in the accumulation of toxic concentrations of the metals within the plant tissue.

Particulate emissions have their greatest impact on terrestrial ecosystems near large emission sources. Particulate matter in itself constitutes a problem only in those few areas where deposition rates are very high. Ecological modification may occur if the particles contain toxic elements, even though deposition rates are moderate. Solubility of particle constituents is critical, since water-insoluble elements are not mobile within the ecosystem. Most of the material deposited by wet and dry deposition on foliar surfaces in vegetated areas is transferred to the soil where accumulation occurs in the litter layer.

7. EFFECTS OF ACIDIC DEPOSITION ON TERRESTRIAL ECOSYSTEMS

7.1 INTRODUCTION

Determining the effects of acidic precipitation on terrestrial ecosystems is not an easy task. In aquatic ecosystems, it has been possible to measure decreases in pH and then observe the response of organisms living in aquatic ecosystems to acidification. In the case of terrestrial ecosystems, the situation is more complicated since no components of terrestrial ecosystems appear to be as sensitive to a change in pH as organisms living in poorly buffered aquatic ecosystems. In addition, indirect effects may only be expressed after long periods of time. Nonetheless, the possibility exists that soils and vegetation may be affected, directly or indirectly, by acidic precipitation, albeit in complex ways.

Occurrence of acidic precipitation (rain and snow) in many regions of the United States, Canada, and Scandanavia appears to possess the potential for impoverishing sensitive soils, degrading natural areas, injuring forests, and damaging stone monuments and buildings.

Sulfur and nitrogen oxides, emitted through the combustion of fossil fuels, have been implicated as the chief contributors to the acidification of precipitation. The fate of sulfur and nitrogen oxides, as well as other pollutants emitted into the atmosphere, depends on their dispersion, transport, transformation, and deposition. Emissions from automobiles occur at ground level, those from electric power generators from smoke stacks 300 meters (1000 feet) or more in height. Transport and transformation of the sulfur and nitrogen oxides are in part associated with the height at which they are emitted. The greater the height, the greater the likelihood of a longer residence time in the atmosphere and a greater opportunity for chemical transformation of the oxides to sulfates, nitrates or other compounds. Ozone and other photochemical oxidants are believed to be involved in the chemical transformations. Because of long range transport, acidic precipitation in a particular site or regions can be the result of emissions from sources in states or regions hundreds of miles away rather than local sources. To date the complex nature of the chemical transformation processes has not made possible the demonstration of a direct cause and effect relationship between emissions of sulfur and nitrogen oxides and the acidity of precipitation.

Natural emissions of sulfur and nitrogen compounds are also involved in the formation of acidic precipitation; however, in industrialized regions anthropogenic emissions exceed natural emissions.

Precipitation is arbitrarily defined as being acidic if its pH is less than 5.6. Currently the acidity of precipitation in the Northeastern United States, the region most severely impacted, ranges from pH 3.0 to 5.0. Precipitation episodes with a pH as low as 3.0 have been reported from other regions of the United States. The pH of precipitation can vary from event to event, from season to season and from geographical area to geographical area.

The impact of acidic precipitation on aquatic and terrestrial ecosystems is not the result a single or several precipitation events, but the result of continued additions of acids or acidifying substances over time. Wet deposition of acidic substances on freshwater lakes, streams, and natural land areas is only part of the problem. Acidic substances exist in gases and particulate matter transferred into the lakes, streams, and land areas by dry deposition. Therefore all the observed biological effects should not be attributed to acidic precipitation alone.

Sensitivity of a lake to acidification depends on the acidity of both wet and dry deposition, the soil system of the drainage basin, canopy effects of ground cover and the composition of the watershed bedrock.

Acidic precipitation may indirectly influence terrestrial plant productivity by altering the supply and availability of soil nutrients. Acidification increases leaching of plant nutrients (such as calcium, magnesium, potassium, iron, and manganese), increased the rate of weathering of most minerals, and also makes phosphorus less available to plants. Acidification also decreases the rate of many soil microbiological processes such as nitrogen fixation by Rhizobium bacteria on legumes and by the free-living Azotobacter, mineralization of nitrogen from forest litter, nitrification of ammonium compounds, and overall decay rates of forest floor litter.

Plants usually take up sulfur in the form of sulfate from the soil; however, they can also take up SO_2 from the atmosphere through their leaves and utilize it as a sulfur souce for plant nutrition. If soil sulfur is low, plants may obtain most of their required sulfur from the atmosphere. Though small amounts of SO_2 may be beneficial, large amounts and high frequency of uncontrolled applications can be detrimental in the long term.

At present, there are no documented observations or measurements of changes in natural terrestrial ecosystems that can be directly attributed to acidic precipitation. This does not necessarily indicate that none are occurring. The information available on vegetational effects is an accumulation of the results of a wide variety of controlled research approacheds largely in the laboratory, using in most instances some form of "simulated" acidic rain, frequently dilute sulfuric acid and/or nitric acid. The simulated "acid rains" have deposited hydrogen (H^+), sulfate ($SO_4^=$) and nitrate (NO_3^-) ions on vegetation and have caused necrotic lesions in a wide variety of plants species under greenhouse and laboratory conditions. Such results must be interpreted with caution, however, because the growth and morphology of leaves under greenhouse conditions are often atypical of field conditions. Based on laboratory studies, sensitivity of plants to acidic depositions seems to be associated with the wettability of leaf surfaces. The shorter the time of contact, the lower the resulting dose, and the less likelihood of injury.

7.2 EFFECTS ON SOILS

Acidity is a critical factor in the behavior of natural or agricultural soils. Soil acidity influences the availability of plant nutrients and various microbiological processes which are necessary for the functioning of terrestrial ecosystems; therefore, there is concern that acidic precipitation over time could have an acidifying effect on soils through the addition of hydrogen ions. As water containing hydrogen cations (usually from weak acids) moves through the soil, some of the hydrogen ions replace adsorbed exchangeable cations, such as Ca^{++}, Mg^{++}, K^+, and Na^+ (see Figure 7-1). The removed cations are then carried deep into the soil profile or into the ground water. In native soils hydrogen ions are derived from the following sources (Wiklander, 1979):

1. nutrient uptake by plants--the roots adsorb cation nutrients and desorb H^+;
2. CO_2 produced by plant roots and micro-organisms;
3. oxidation of NH_4^+ and S, FeS_2, and H_2S to HNO_3 and H_2SO_4;
4. very acid litter in coniferous forests, the main acidifying source for the A and B horizons;
5. atmospheric deposition of H_2SO_4 and some HNO_3, NO_x, HCl and NH_4^+ (after nitrification to HNO_3).

In addition to the acidifying factors listed above, the use of ammonium fertilizers on cultivated lands increases the hydrogen cations in the water solution. Ammonium fertilizers are oxidized by bacteria to form nitrate (NO_3^-) and hydrogen ions (H^+) (Donahue et al., 1977). Increased leaching causes soils to become lower in basic Ca^{++}, Mg^{++}, Na^+, and K^+ cations (Donahue et al., 1977). Sensitivity to leaching is according to the following sequence: $Na^+ >> K^+ > Mg^{2+} > Ca^{2+}$ (Wiklander, 1979).

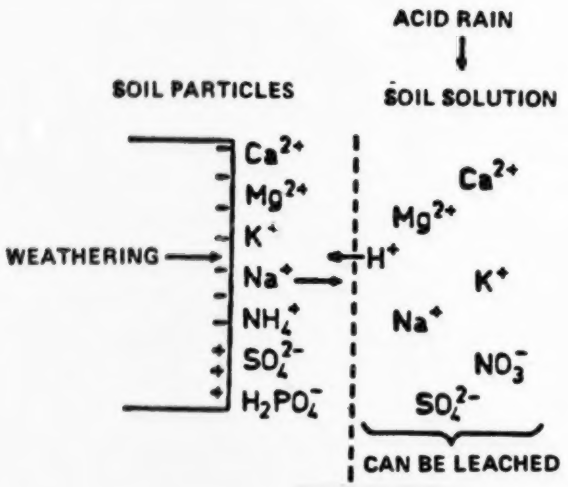


Figure 7-1. Showing the exchangeable ions of a soil with pH 7, the soil solution composition, and the replacement of Na^+ by H^+ from acid rain.

Source: Wiklander (1979).

Norton (1977) cited the potential effects of acidic deposition on soils, Table 7-1. Of those listed, only the increased mobility of cations and their accelerated loss has been observed in field experiments. Overrein (1972) observed an increase in calcium leaching under simulated acid rain conditions and increased loss by leaching of Ca^{++}, Mg^{++}, and Al^{+3} were observed by Cronan (1980) when he treated New Hampshire soils with simulated acid rain at a pH 4.4.

Wiklander (1979) notes that in humid areas leaching leads to a gradual decrease of plant nutrients in available and mobilizable forms. The rate of nutrient decrease is determined by the buffering capacity of the soil and the amount and composition of precipitation (pH and salt content). Leaching sooner or later leads to soil acidification unless the buffering capacity of the soil is great and/or the salt concentration of precipitation is high. Soil acidification influences the amount of exchangeable nutrients and is also likely to affect various biological processes in the soil.

Acidic precipitation increases the amounts of SO_4^{2-} and NO_3^- entering the soils. Nitrate is easily leached from soil; however, because it is usually deficient in the soil for both plants and soil microorganisms, it is rapidly taken up and retained within the soil-plant system (Abrahamsen and Dollard, 1979; Abrahamsen et al., 1976; Gjessing et al., 1976). The fate of sulfate is determined by its mobility. Retention of sulfate in soils appears to depend on the amount of hydrous oxides of iron and aluminum present. The amounts of these compounds present varies with the soil type. Insignificant amounts of the hydrated oxides of iron (Fe) and aluminum (Al) are found in organic soils; therefore, sulfate retention is low (Abrahamsen and Dollard, 1979). The presence of hydrated oxides of iron and aluminum, however, is only one of the factors associated with the capability of a soil to retain sulfur. The capacity of soils to adsorb and retain anions increases as the pH decreases and with the salt concentration. Polyvalent anions of soluble salts added experimentally to soils in-

TABLE 7-1. POTENTIAL EFFECTS OF ACID PRECIPITATION ON SOILS

Effect	Comment
Increased mobility of most elements	Mobility changes are essentially in the order: monovalent, divalent, trivalent cations.
Increased loss of existing clay minerals	Under certain circumstances may be compensated for by production of clay minerals which do not have essential (stoichiometric) alkalies or alkali earths.
A change in cation exchange capacity	Depending on conditions, this may be an increase or a decrease.
A general proportionate increase in the removal of all cations from the soil	In initially impoverished or unbuffered soil, the removal may be significant on a time scale of 10 to 100 years.
An increased flux in nutrients through the ecosystem below the root zone	

Source: Norton (1977).

crease adsorption and decrease leaching of salt cations. The effectiveness of the anions studied in preventing leaching increased in the following order: $Cl^- \sim NO_3^- < SO_4^{2-} < H_2PO_4^-$ (Wiklander, 1980). Additions of sulfuric acid to a soil will have no effect on cation leaching unless the sulfate anion is mobile, as cations cannot leach without associated anions (Johnson et al. 1980; Johnson, 1980; Johnson and Cole, 1980).

Leaching of soil nutrients is efficiently inhibited by vegetation growing on it. Plant roots take up the nutrients frequently in larger amounts than required by the plants. Large amounts of these nutrients will later be deposited on the soil surface as litter or as leachate from the vegetation canopy (Abrahamsen and Dollard, 1979).

In lysimeter experiments in Norway, plots with vegetation cover were used. One plot had a dense layer of the grass, Deschampsia flexuosa (L.) Trin. and the other a less dense cover. The soil retained approximately 50 percent of the SO_4^{2-} added to it. The greatest amount was retained in the lysimeters covered with grass; the relative retention increased with increasing additions of sulfate (Abrahamsen and Dollard, 1979). Leaching of cations from the soil was reduced by the retention of the SO_4^{2-}; however, leaching of Ca^{2+} and Mg^{2+} increased significantly as the acidity of the simulated rain increased. In the most acid treatment leaching of Al was highly significant. The behavior of K^+, NO_3^-, and NH_4^+ was different in the two lysimeter series. These ions were retained in the grass-covered lysimeters whereas there was a net leaching of K^+ and NO_3^- in the other series. Statistically significant effects were obtained only when the pH of the simulated rain was 3.0 or lower (Abrahamsen and Dollard, 1979).

The Scandinavian lysimeter experiments appear to demonstrate that the relative rate of adsorption of sulphate increases as the amounts applied are increased. In the control lysimeters the output/input ratio was approximately one. These results are in agreement with results of watershed studies which frequently appear to demonstrate that, on an annual basis, sulfate outflow is equal to or greater than the amounts being added (Abrahamsen and Dollard, 1979; Gjessing et al., 1976). Increased outflow may be attributed to dry deposition and the weathering of sulfur-bearing rocks. The increased deposition of sulfate via acidic precipitation appears to have increased the leaching of sulfate from the soil. Together with the retention of hydrogen ions in the soil this results in an increased leaching of the nutrient cations K^+, Ca^{2+}, and Mg^{2+}, Mn (Abrahamsen and Dollard, 1979). Shriner and Henderson (1978), however, in their study of sulfur distribution and cycling in the Walker Branch Watershed in eastern Tennessee noted the additions of sulfate sulfur by precipitation were greater than the amount lost in stream flow. Analysis of the biomass and soil concentrations of sulfur indicated that sulfur was being retained in the mineral soil horizon. It is suggested that leaching from organic soil horizons may be the mechanism by which sulfur is transferred to the mineral horizon. Indirect evidence suggests that vegetation scavenging of atmospheric sulfate plays an important role by adding to the amounts of sulfur entering the forest system over wet and dry deposition.

Studies of the nutrient cycling of sulfur in a number of forest ecosystems indicate that some ecosystems accumulate (Johnson et al., 1980; Shriner and Henderson, 1978; Heinrichs and Mayer, 1977) while other ecosystems maintain a balance between the additions and losses of sulfur or show a net loss (Cole and Johnson, 1977). Sulfur accumulation appears to be associated with sulfate adsorption in subsoil horizons. Sulfate adsorption is strongly dependent on pH. Little adsorption occurs above pH 6-7 (Harward and Reisenaur, 1966). The amount of sulfate in a soil is a function of a soil's adsorption properties and the amount of sulfate that has been added to the soil, integrated over time. Soil properties may favor the adsorption of sulfate; however, the net annual accumulation of sulfate at any specific time will be influenced by the degree of soil saturation (Johnson et al., 1980).

Lowered soil pH also influences the availability and toxicity of metals to plants. In general, potentially toxic metals become more available as pH decreases. Ulrich (1975) reported that aluminum released by acidified soils could be phytotoxic if acid rain continued for a long period. The degree of ion leaching increased with decreases in pH, but the amount of cations leached was far less than the amount of acid added (Malmer, 1976). Baker et al. (1977) found that sulfur dioxide in precipitation increased the extractable acidity and aluminum, and decreased the exchangeable bases, especially calcium and magnesium. Although dilute sulfuric acid in sandy podsolic soils caused a significantly decreased pH of the leached material, the amount of acid applied (not more than twice the yearly airborne supply over southern Scandinavia) did not acidify soil as much as did nitrate fertilizer (Tamm et al., 1977). Highly acidic rainfall, frequently with a pH less than 3.0, in combination with heavy metal particulate fallout from smelters, has caused soils to become toxic to seedling survival and establishment according to observations by Hutchinson and Whitby (1976). Very low soil pH's are associated with mobility of toxic aluminum compounds in the soils. High acidity, high sulfur, and heavy metals in the rainfall have caused fundamental changes in the structure of soil organic matter. The sulfate and heavy metals were borne by air from the smelters in the Sudbury area of Ontario and brought to earth by dry and wet deposition. Among the metals deposited in rainfall and dustfall were nickel, copper, cobalt, iron, zinc, and lead. Most of these metals are retained in the upper layers of soil, except in very acid or sandy soils.

The accumulation of metals in soils is mainly an exchange phenomenon. Organic components of litter, humus, and soil may bind heavy metals as stable complexes (Tyler, 1972). The heavy metals when bound may interfere with litter decay and nutrient cycling, and in this manner interfere with ecosystem functioning (Tyler, 1972). Acidic precipitation, by altering the equilibria of the metal complexes through mobilization, may decrease the residence time of the heavy metals in soil and litter (Tyler, 1977, 1972).

Biological processes in the soil necessary for plant growth can be affected by soil acidification. Nitrogen fixation, decomposition of organic material, and mineralization, especially of nitrogen, phosphorus and sulfur, could be affected (Alexander, 1980; Abrahamsen and Dollard, 1979; Tamm et al., 1977; Malmer, 1976). Nearly all of the nitrogen, most of the phosphorus and sulfur, as well as other nutrient elements in the soil are bound in organic combination. In this form, the elements are largely or entirely unavailable for utilization by higher plants (Alexander, 1980). It is principally through the activity of heterotrophic microorganisms that nitrogen, phosphorus, and sulfur are made available to the autotrophic higher plants. Thus, the microbial processes that lead to the conversion of the organic forms of these elements to the inorganic state are crucial for maintaining plant life in natural or agricultural ecosystems. The key role of these degradative processes is illustrated by the fact that nitrogen is limiting for food production in much of the world and governs primary productivity in many terrestrial habitats (Alexander, 1980).

Many, and probably most, microbial transformations in soil may be brought about by several species. Therefore, the reduction or elimination of one population is not necessarily detrimental since a second population, not affected by the stress, may fill the partially or totally vacated niche. On the other hand, there are a few processes that are carried out, so far as it is now known, by only a single species, and elimination of that species could have serious consequences. Examples of this are nitrification in which ammonium is converted to nitrate, and nodulation of leguminous plants, for which the bacteria are reasonably specific according to the leguminous host (Alexander, 1980).

Nitrification is one of the best indicators of pH stress because the responsible organisms, presumably largely autotrophic bacteria, are sensitive both in culture and in nature to increasing acidity (Dancer et al., 1973). Although nitrification will sometimes occur at pH values below 5.0, characteristically the rate decreases with increasing acidity and often is undetectable much below pH 4.5. Limited data suggest that the process of sulfate reduction to sulfide in soil is markedly inhibited below a pH of 6.0. (Connell and Patrick, 1968) and studies of the presumably responsible organisms in culture attest to the inhibition linked with the acid conditions (Alexander, 1980).

It is difficult to make generalizations concerning the effects of soil acidification on microorganisms. Many microbial processes that are important for plant growth are clearly suppressed as the pH declines; however, the inhibition noted in one soil at a given pH may not be noted at the same pH in another soil (Alexander, 1980). The capacity of some microorganisms to become acclimated to changes in pH suggests the need to study this phenomenon using environments that have been maintained at different pH values for some time. Typically the studies have been done with soils maintained only for short periods at the greater acidity (Alexander, 1980). The consequences of increased acidity in the subterranean ecosystem are totally unclear, however; the pH of soil influences not only the microbial community at large, but also those specialized populations that colonize the root surfaces (Alexander, 1980).

The addition of nitrate and other forms of nitrogen from the atmosphere to ecosystems through the activity of microorganisms is an integral function of the terrestrial nitrogen cycle. The contribution of inorganic nitrogen in wet precipitation (rain plus snow) is usually equivalent to only a few percent of the total nitrogen assimilated annually by plants in terrestrial ecosystems; however, total nitrogen contributions, including organic nitrogen, in bulk precipitation (rainfall plus dry fallout) can be significant, especially in unfertilized natural systems.

Atmospheric contributions of nitrate can range from less than 0.1 kg N/ha/yr in the Northwest (Fredricksen, 1972) to 4.9 kg N/ha/yr in the Eastern United States (Henderson and Harris, 1975; Likens et al, 1970). Inorganic nitrogen (ammonia-N plus nitrate-N) additions in wet precipitation ranged from less than 0.5 kg/ha/yr to more than 3.5 kg/ha/yr in Junge's (1958) study of rainfall over the United States. On the other hand, total nitrogen loads in bulk precipitation range from less than 5 kg/ha/yr in desert regions of the West to more than 30 kg/ha/yr near barnyards in the Midwest. Total contributions of nitrogen from the atmosphere commonly range from about 10 to 20 kg N/ha/yr for most of the United States (National Research Council, 1978c).

In comparison, rates of annual uptake by plants range from 11 to 125 kg N/ha/yr in ecosystems selected from several bioclimatic zones (National Research Council, 1978). Since the lowest additions are generally associated with desert areas where rates of uptake by plants are low, and the highest additions usually occur in moist areas where plant uptake is high, the contributions of ammonia and nitrate from rainfall to terrestrial ecosystems are equivalent to about 1 to 10 percent of annual plant uptake. In eastern deciduous and western coniferous forest ecosystems, contributions from bulk precipitation, on the other hand, represent from about 8 to 25 percent of the annual plant requirements. Although these comparisons suggest that plant growth in terrestrial ecosystems depends to a significant extent on atmospheric deposition, it is not yet possible to estimate the importance of these contributions by comparing them with the biological fixation and mineralization of nitrogen in the soil. In nutrient-impoverished ecosystems, such as badly eroded abandoned croplands or soils subjected to prolonged leaching by acidic precipitation, nitrogen additions from atmospheric depositions are certainly important to biological productivity. In largely unperturbed forests, recycled nitrogen from the soil organic pool is the chief source of nitrogen for plants, but nitrogen to support increased production must come either from biological fixation or from atmospheric contributions. It seems possible, therefore, that man-generated contributions could play a significant ecological role in a relatively large portion of the forested areas near industrialized regions (Galloway, 1978).

Sulfur, like nitrogen, is essential for optimal plant growth. Plants usually obtain sulfur from the soil in the form of sulfate. The amount of mineral sulfur in soils is usually low and its release from organic matter during microbial decomposition is a major source for plants (Donahue et al., 1977). Another major source is the wet and dry deposition of atmospheric sulfur (Donahue et al., 1977; Jones, 1975; Brady, 1974).

In agricultural soils crop residues, manure, irrigation water, fertilizers, and soil amendments are important sources of sulfur. The amounts of sulfur entering the soil system from atmospheric sources is dependent on proximity to industrial areas, the sea coast, and marshlands. The prevailing winds and the amount of precipitation in a given region are also important (Halstead and Rennie, 1977). Near fossil-fueled power plants and industrial installations the amount of sulfur in precipitation may be as much as 150 pounds per acre (168 kg/ha) or more (Jones, 1975). By contrast, in rural areas, based on the equal distribution of sulfur oxide emissions over the coterminous states, the amount of sulfur in precipitation is generally well below the average 15 pounds per acre (17 kg/ha). Approximately 5 to 7 pounds per acre (7 to 8 kg/ha) per year were reported for Oregon in 1966 (Jones, 1975). Shinn and Lynn (1979) have estimated that in the Northeastern United States, the area where precipitation is most acidic, approximately 5 x 10^6 tons of sulfate per year is removed by rain. Hoeft et al. (1972) estimated the overall average sulfur as sulfate deposition at 26 pounds of sulfur/acre per year (30 kg S/ha per year). Estimates for rural areas were 14 pounds of sulfur per acre per year (16 kg/ha/yr). Approximately 40 to 50 percent of the sulfur additions occurred from November to February. Tabatabai and Laflin (1976) found that SO_4-S deposition in Iowa was greatest in fall and winter when precipitation was low.

Experimental data have shown that even though plants are supplied with adequate soil sulfate they can absorb 25 to 35 percent of their sulfur from the atmosphere (Brady, 1974). Particularly if the soil sulfur is low and atmosphere sulfur high, most of the sulfur required by the plant can come from the atmosphere (Brady, 1974). Atmospheric sulfur would be of benefit chiefly to plants growing on lands with a low sulfur content (Brezonik, 1976).

Tree species vary in their ability to utilize sulfur. Nitrogen and sulfur are biochemically associated in plant proteins, therefore, a close relationship exists between the two in plants. Apparently, nitrogen is only taken up at the rate at which sulfur is available. Protein formation, therefore, is limited by the amount of sulfur available (Turner and Lambert, 1980). Conifers accumulate as sulfate any sulfur beyond the amount required to balance the available nitrogen. Protein formation proceeds at the rate at which nitrogen becomes available. Trees are not injured when sulfur is applied as sulfate rather than SO_2 (Turner and Lambert, 1980).

When discussing the effects of acidic precipitation, or the effects of sulfates or nitrates on soils, a distinction should be made between managed and unmanaged soils. There appears to be general agreement that managed agricultural soils are less susceptible to the influences of acidic precipitation than are unmanaged forest or rangeland soils. On managed soils more than adequate amounts of lime are used to counteract the acidifying effects of fertilizers in agricultural soils. Ammonium fertilizers, usually as ammonium sulfate $[(NH_4)_2SO_4]$ or ammonium nitrate, (NH_4NO_3) are oxidized by bacteria to form sulfate (SO_4^{2-}) and/or nitrate (NO_3^-) and hydrogen ions (H^+) (Donahue et al. 1977; Brady, 1974). The release of hydrogen ions into the soil causes the soil to become acidified. Hydrogen ions are also released into the soil when plants take up mineral nutrients. Hence, substances (notably various complexes of ammonium and sulfate ions), although of neutral pH, or nearly so, are acidifying in their effects when they are taken up by plants or animals. Thus, the concept of "acidifying precipitation" must be added to the concept of "acid precipitation."

The acidifying effects of fertilization or acidic precipitation is countered in managed soils through the use of lime. Liming raises the pH and thereby eliminates most major problems associated with acidic soils (Donahue et al., 1977; Likens et al., 1977). Liming all natural soils sensitive to acidification would be cost-prohibitive as well as extremely difficult to carry out.

Precipitation adds many chemicals to terrestrial, aquatic, and agricultural ecosystems. In addition to sulfur and nitrogen, phosphorus and potassium are biologically most important because they often are in limited supply in the soil (Likens et al., 1977). Other chemicals of varying biological importance and varying concentration found in precipitation over North America are the following: chlorine, sodium, calcium, magnesium, iron, nickel, copper, zinc, cadmium, lead, manganese (Beamish, 1976; Hutchinson and Whitby, 1976; Brezonik, 1976), mercury (Brezonik, 1976), and cobalt (Hutchinson and Whitby, 1976). Rain over Britain and the Netherlands, according to Gorham (1976), contained the following elements in addition to those reported for North American precipitation: aluminum, arsenic, beryllium, cerium, chromium, cesium, antimony, scandium, selenium, thorium, and vanadium. Again, it is obvious that many of these elements will be found in precipitation in highly industrialized areas and will not be of biological importance until they enter an ecosystem where they may come into contact with some form of life, as in the case of heavy metals in the waters and soils near Sudbury, Ontario. Of the chemical elements found in precipitation, magnesium, iron, copper, zinc, and manganese are essential in small amounts for the growth of plants; however, at high concentrations these elements, as well as the other heavy metals, can be toxic to plants and animals. Furthermore, the acidity of precipitation can affect the solubility, mobility, and toxicity of these elements to the foliage or roots of plants and to animals or microorganisms that may ingest or decompose these plants.

Wiklander (1979) has pointed out that based on the ion exchange theory, ion exchange experiments, and the leaching of soil samples, the following conclusions can be drawn about the acidifying effect on soils through the atmospheric deposition of mineral acids.

1. At a soil pH > 6.0 acids are fully neutralized by decomposition of $CaCO_3$ and other unstable minerals and by cation exchange.
2. At soil pH < 5.5 the efficiency of the proton to decompose minerals and to replace exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+ decreases with the soil pH. Consequently, the acidifying effect of mineral acids on soils decreases, but the effect on the runoff water increases in the very acid soils.
3. Salts of Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ in the precipitation counteract the absorption of protons and, in that way, the decrease of the base saturation. A proportion of the acids percolate through the soil and acidify the runoff.

The sensitivity of various soils to acidic precipitation depends on the soil buffer capacity and on the soil pH. Noncalcareous sandy soils with pH > 5 are the most sensitive to acidification; however, acidic soils would be most likely to release aluminum.

Very acid soils are less sensitive to further acidification because they are already adjusted by soil formation to acidity and are therefore more stable. In these soils easily weatherable minerals have disappeared, base saturation is low, and the pH of the soil may be less than that of precipitation. The low nutrient level is a crucial factor which limits productivity in these soils. Even a slight decrease in nutrient status by leaching may have a detrimental effect on plant yield (Wiklander, 1979). Fertilization appears to be the only preventive measure.

In properly managed cultivated soils, acidic precipitation should cause only a slight increase in the lime requirement, with a cost compensated for by the supply of sulfur, nitrogen, magnesium, potassium, and calcium made available to plants (Wiklander, 1979).

A report by Hendrey et al. (1980b) compared pre-1970 data with post-1975 data. A marked decline in both alkalinity and pH of the waters of North Carolina and New Hampshire sensitive to acidification was noted. In the former, pH and alkalinity have decreased in 80 percent of the streams tested and in the latter pH has decreased 90 percent since 1949 in the streams tested. These areas are predicted to be sensitive by geological mapping on the basis of their earlier alkalinity values. Detailed county by county maps of other states in the eastern United States suggest the sensitivity of these regions to acidic precipitation.

Though bedrock geology generally is a good predictor of the susceptibility of an area to acidification due to acidic precipitation, other factors also have an influence. Florida, for example, is underlaid by highly calcareous and phosphate rock, suggesting that acidification of lakes and streams is highly unlikely. Many of the soils, however, (particularly in northern Florida), are very mature and have been highly leached of calcium carbonate, and, as a result, some lakes in which groundwater inflow is minimal have become acidified (Hendry and Brezonik, 1980). Conversely, there are areas in Maine with granitic bedrock where lakes have not become acidified, despite receiving precipitation with an average pH of approximately 4.3, because the drainage basins contain lime-bearing till and marine clay (Davis et al., 1978). Small amounts of limestone in a drainage basin exert a strong influence on water quality in terrain which would otherwise be vulnerable to acidification. Soils in Maine in the areas where the pH of lakes has decreased due to acidic precipitation are immature, coarse, and shallow and are derived largely from granitic material and commonly have a low capacity for assimilating hydrogen ions from leachate and surface runoff in lake watersheds (Davis et al., 1978). The occurrence of limestone outcroppings in the Adirondack Mountains of New York State are highly correlated with lake pH levels. The occurrence of limestone apparently counteracts any effects of acidic precipitation. Consequently, when predicting vulnerability of a particular region to acidification, a careful classification of rock mixtures should be made. Rock formations should be classified according to their potential buffering capacity, and the type of soil overlying the formations should be noted. Local variations in bedrock and soils are very important in explaining variations in acidification between lakes within an area.

7.3 TERRESTRIAL ECOSYSTEMS

Predicting the sensitivity of terrestrial ecosystems to acidic precipitation is much more difficult than for aquatic ecosystems. With aquatic ecosystems it is possible to compare affected and unaffected ecosystems and note where the changes have occurred. With terrestrial ecosystems, comparisons are difficult to make because the effects of acidic precipitation have been difficult to detect. Therefore, predictions regarding the sensitivity of terrestrial ecosystems must, as much as possible, use the data which link the terrestrial ecosystems to aquatic ecosystems, i.e., the data on bedrock geology. Since, in most regions of the world, bedrock is not exposed but is covered with soil, it is the sensitivity of different types of soil which must be assessed. Therefore, the first step is to define "sensitivity" as it is used here in relation to soils and acidic precipitation. Sensitivity of soils to acidification alone, though it may be the most important long-term effect, is too narrow a concept. Soils influence the quality of waters in associated streams and lakes and may be changed in ways other than simple pH-base saturation relationships, e.g., microbiological populations of the surface layers, accelerated loss of aluminum by leaching. Therefore, criteria need to be used that would relate soil "sensitivity" to any important change brought about in the local ecosystem by acid precipitation (McFee, 1980).

All soils are not equally susceptible to acidification. Sensitivity to leaching and to loss of buffering capacity varies according to the type of parent material from which a soil is derived. Buffering capacity is greatest in soils derived from sedimentary rocks, especially those containing carbonates, and least in soils derived from hard crystalline rocks such as granites and quartzites (Gorham, 1958). Soil buffering capacity varies widely in different regions of the country. Unfortunately, many of the areas now receiving the most acidic precipitation also are those with relatively low natural buffering capacities.

The buffering capacity of soil depends on mineralogy, texture, structure, organic matter, pH, base saturation, salt content, and soil permeability. Above a pH of 5.5 virtually all of the H^+ ions, irrespective of source, are retained by ion exchange and chemical weathering. Below pH 5.5, the retention of the H^+ ion decreases with the soil pH in a manner determined by the composition of the soil (Donahue et al., 1977). With a successive drop in the soil pH below 5.0, an increasing proportion of hydrogen ions (H^+) and deposited sulfuric acid will pass through the soil and acidify runoff water (Donahue et al., 1977). The sensitivity of different soils based on pH, texture, and calcite content is summarized in Table 7-2.

TABLE 7-2. THE SENSITIVITY TO ACID PRECIPITATION BASED ON: BUFFER CAPACITY AGAINST pH-CHANGE, RETENTION OF H^+, AND ADVERSE EFFECTS ON SOILS

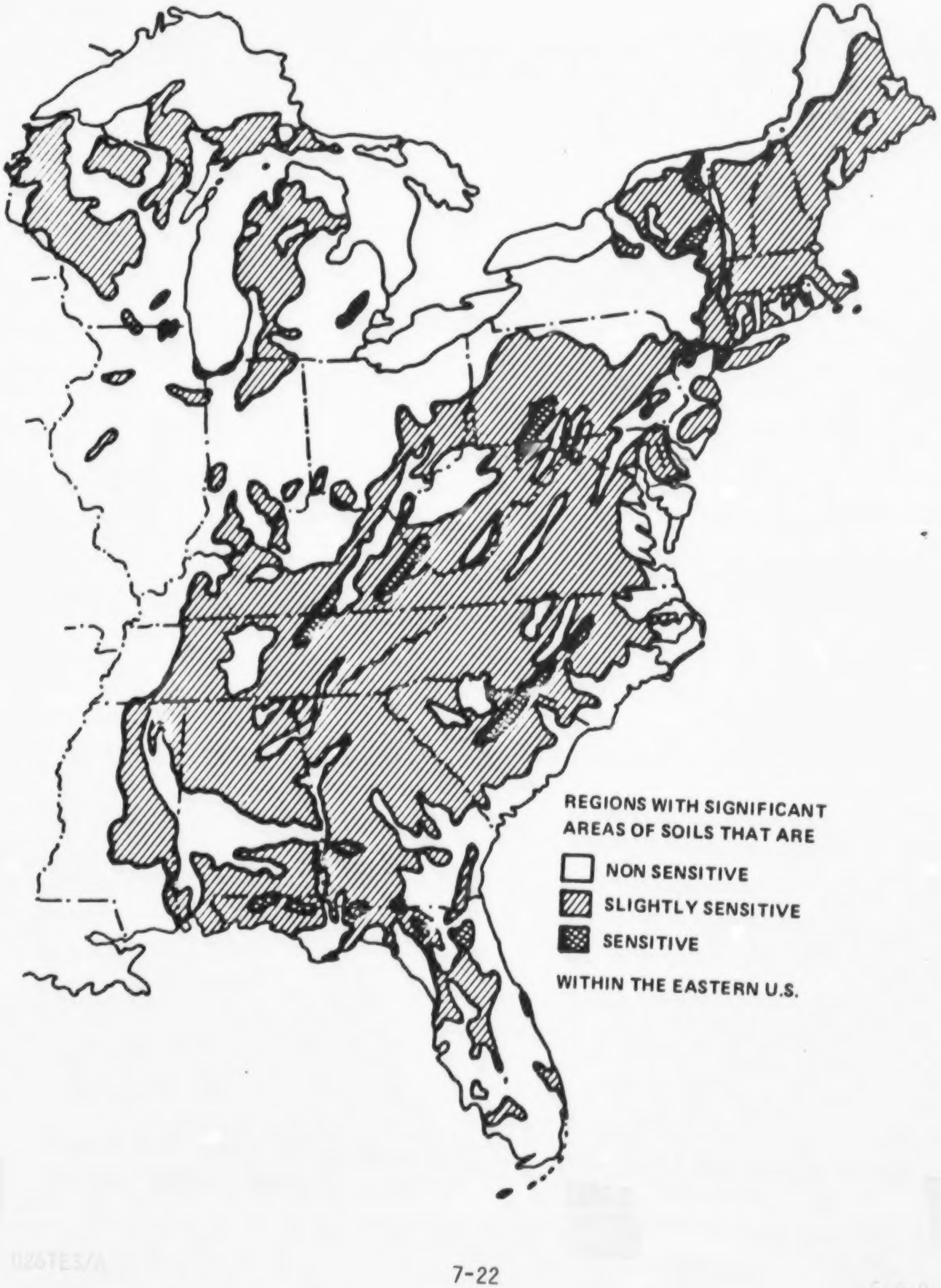
	Calcareous soils	Noncalcareous clays pH > 6	Noncalcareous sandy soils pH > 6	Cultivated soils pH > 5	Acid soils pH < 5
Buffering	Very high	High	Low	High	Moderate
H^+ retention	Maximal	Great	Great	Great	Slight
Adverse effects	None	Moderate	Considerable	None - slight	Slight

Source: Wiklander (1979).

Soils are the most stable component of a terrestrial ecosystem. Any changes which occur in this component would probably have far-reaching effects. McFee (1980) has listed four parameters which are of importance in estimating the sensitivity of soils to acidic precipitation. They are:

1. the total buffering or cation exchange capacity which is provided primarily by clay and soil organic matter.
2. the base saturation of that exchange capacity which can be estimated from the pH of the soil.
3. the management system imposed on the soil; is it cultivated and amended with fertilizers or lime or renewed by flooding or by other additions?
4. the presence or absence of carbonates in the soil profile.

McFee (1980) mapped the soils of the Eastern United States and included effects of cultivation (Figure 7-2). The areas containing most of the soils potentially sensitive to acidic precipitation are in the upper Coastal Plain and Piedmont regions of the southeast, along the Appalachian Highlands, through the east central and northeastern areas, and in the Adirondack Mountains of New York (McFee, 1980). The current limited state of knowledge regarding the effects of acidic precipitation on soils makes a more definitive judgment of the location of areas with the most sensitive soils difficult at the present time.


REGIONS WITH SIGNIFICANT
AREAS OF SOILS THAT ARE
NON SENSITIVE
SLIGHTLY SENSITIVE
SENSITIVE
WITHIN THE EASTERN U.S.

The capacity of soils to absorb and retain anions, also important in determining whether soils will become acidified, was not discussed by McFee (1980). The capacity for anion absorption is great in soils rich in hydrated oxides of aluminum (Al) and iron (Fe). Reduced leaching of salt cations is of great significance not only in helping to prevent soil acidification but in geochemical circulation of nutrients, fertilization in agriculture and preventing water pollution (Wiklander, 1980; Johnson et al. 1980; Johnson, 1980). This parameter, as well as those listed by McFee (1980), should be used in determining the sensitivity of soils to acidification by both wet and dry deposition.

8. SUMMARY OF EFFECTS OF ATMOSPHERIC CONTAMINANTS ON TERRESTRIAL ECOSYSTEMS

Terrestrial ecosystems are delicately balanced associations of plant and animal populations that are in continuous harmony with their environment. Every environmental component has some degree of influence on each population, and this influence may increase or decrease according to the relative magnitude or quantity of the component. When there is a deficiency of an essential component, such as a required nutrient, one or more populations are disrupted and the ecosystem is said to be perturbed. It is also a characteristic of environmental components that they may be present in excess, even those which are required. Ecosystem perturbation may occur by a deficiency of a required component or an excess of any component. Perturbations may also result from the effects of two or more components which may be additive (sum of each effect equals total combined effect), less-than-additive or greater-than-additive. Effects that are greater-than-additive are often called synergistic effects. Recovery of the ecosystem depends on the persistency of the perturbation and the ability of the affected populations to adapt. When populations are eliminated, ecosystem recovery rests on the availability of a new population to fill the vacant niche.

The effect that an environmental component has on a population is a function of its magnitude and duration. In terms of a pollutant, this is referred to as a "dose", or the concentration times the period of exposure. The effect is quantified in terms of a response, which may be visible damage or apparent reduction in growth. Visible damage to plant leaves usually occurs as "chlorosis", or yellowing of the leaves that indicates a breakdown in the photosynthetic mechanisms; necrosis, or death of leaf tissue, is another visible sign of injury that appears as distinct yellow or brown spots on the leaf surface.

Growth reduction is usually difficult to quantify. For vegetation, growth is the addition of new tissue to roots, stems, leaves or fruits. It is not uncommon for one plant part to grow at the expense of another. Thus, by inhibiting fruit production, a pollutant may cause an apparent increase in leaf production. The common denominator for most plant responses is the effect of the pollutant on photosynthesis, which may be chlorosis in the breakdown of chlorophyll, necrosis in the death of photosynthetically active tissue, or growth reduction resulting from a reduced photosynthetic output.

Atmospheric contaminants are just one group of environmental components that can perturb an ecosystem. The most common contaminants are ozone, nitrogen oxides, sulfur oxides, and contaminants associated with particulate matter. At low concentrations, nitrogen oxides and sulfur oxides can be nutritive and thus have a fertilizer effect on ecosystems deficient in nitrogen or sulfur. Atmospheric nitrogen and sulfur are also associated with nitric and sulfuric acid, which are the main components of acid precipitation. Ozone, nitrogen oxides, and sulfur oxides are found primarily in the gas phase.

Ozone is a natural component of the upper atmosphere, but in the troposphere, this gas can have a harmful effect on vegetation. Along with peroxylacylnitrate (PAN) and nitrogen dioxide, ozone is classified as a photochemical oxidant, or a substance formed in the presence of sunlight, which can destroy biological tissues by oxidizing key metabolic compounds. In sunlight, ozone is produced from the reaction of molecular oxygen with hydrocarbons. It is therefore an indirect product of vehicular emissions. The ambient concentration of ozone depends on its rate of formation, dispersal and removal from the atmosphere. The rate of ozone formation is a function of temperature, sunlight intensity and hydrocarbon concentration. Consequently, ozone concentrations may be highest during periods of greatest plant productivity.

Ozone enters the plant leaf through the stomata and dissolves in the thin film of water surrounding the photosynthetically active mesophyll cells. The immediate effect is to cause an increase in the premeability of the cell membrane. This can disrupt the biochemical pathways and enzyme production systems of the cell, which will eventually disturb the photosynthetic and respiratory processes. If the cell is a guard cell, the ability to remain turgid or flaccid as required would be blocked, and the leaf would not be able to regulate water loss. At the lowest level, there would be a reduction in plant growth, followed by visible foliar injury, increased leaf drop and eventually, death.

Growth reduction in the absence of visible injury can result from physiological disturbances at the cellular and subcellular level. These effects may be reversible. The first response of a single, physiologically active cell to adverse environmental conditions would logically be a reduction in normal activity. In the case of photosynthetic tissue, this mean less photosynthate produced until conditions return to normal. When the adverse conditions are strong oxidants which alter the surface chemistry of the cell membrane, the cell must repair this damage or die. Repair may be effected by neutralizing the effects of the oxidant or by replacing the damaged portion of the cell membrane. At the tissue level, if the cell dies then it must be replaced or there will be a continued reduction in photosynthetic output. When large numbers of cells die, as in necrosis, repair may not be possible within the normal lifetime of the leaf.

From this description, it is reasonable that plant response to ozone depends on dose parameters and the stress status of the plant. Dose is a product of concentration and time, but it is apparent that short exposure to high concentrations may cause more permanent than longer exposure to lower concentration. Frequency of exposure is also important. If a plant is exposed to repeated low doses without sufficient time to recover, the effect may be the same as a single high dose. Stress from other environmental factors, such as insufficient water or less than optimum conditions would seem to lower the plant's resistance to the effects of oxidants. This is not the case, however, as the environmental conditions which are optimum for photosynthetic activity are also those which increase the plant's sensitivity to ozone. A reasonable explanation is that during peak photosynthesis, transpiration is at a maximum and the stomata are open. The leaf is vulnerable to the infiltration of gaseous oxidant molecules.

A reduction in photosynthesis rate can result in other non-visible effects. Root growth may be suppressed, causing a reduction in nutrient uptake and, for some plants, a reduction in nitrogen fixation. Ozone may also affect pollen germination, which can result in reduced reproductive success.

Visible injury is usually to the upper surface of the leaf if the mesophyll tissue is clearly divided into palisade and spongy. Some monocots (grasses and cereals) and a few dicots do not have compartmentalized mesophyll tissue, thus chlorosis or necrosis may be observed on either surface of the leaf. Common names for chlorosis and necrosis vary with the species. Tobacco leaf fleck, grape leaf stipple, white pine tipburn or needle dieback, and ponderosa chlorotic decline are some examples of ozone injury. These same symptoms could be caused by other adverse environmental components which disrupt the photosynthetic mechanism.

Ozone concentrations which can cause growth reduction or damage to plants vary with the type of ecosytem and with the species. Plant populations in a mature forest may be more resistant and may recover faster from ozone exposure than a single population of a crop plant in an agroecosystem. Whereas typical ambient concentrations may be 40 $\mu g/m^3$ (0.02 ppm), growth reduction has been observed between 100 and 200 $\mu g/m^3$ (0.05 and 0.1 ppm) in soybeans, corn, radishes and perhaps wheat. Foliar injury to crops may also occur in the range of 75 to 180 $\mu g/m^3$ (0.04 to 0.09) and to forest vegetation at 120 to 340 $\mu g/m^3$ (0.06 to 0.17 ppm).

Ambient concentrations of ozone have caused damage to forest ecosystems in the Appalachian Mountains of eastern United States and in ponderosa pine forests of southern California. In the Appalachian Mountains, episodes of 160 to 230 $\mu g/m^3$ (0.08 to 0.12 ppm) were sufficient to cause visible foliar damage. In southern California, 40,000 of the 64,000 hectares of ponderosa and Jeffrey pine were moderately to severely affected, representing an estimated 1,300,000 trees. Since 1940, growth reduction attributable to smog from Los Angeles has amounted to 0.2 cm/annual ring thickness. These trees were also found to be more susceptible to infestation by pine bark beetles (*Dendroctonus brevicomis* and *D. ponderosae*). Eastern white pines lose their resistance to the fungi *Lophodermium pinastri* and *Aureobasidium pullulans* following ozone injury. There was a marked deterioration of symbiotic associations with mycorrhizal fungi in ponderosa and eastern white pine.

All of these subtle effects can cause minor perturbations which reverberate throughout the ecosystem. If growth reductions cause decreased productivity of berries, seeds, and leafy vegetation, herbivore and carnivore populations may be affected. Decomposer populations may be affected directly by ozone injury or indirectly by a reduction in litter production. This would reduce the rate and efficiency of nutrient turnover within the ecosystem.

Of the eight nitrogen oxides that may be contaminants of ambient air, nitric oxide (NO) and nitrogen dioxide (NO_2) are the most abundant and the most detrimental. Like ozone, these nitrogen compounds are oxidant gases that enter plant leaves through the stomata and cause injury to photosynthetic tissue. The conditions that control stomatal opening, control the rate of NO_2 uptake.

Growth reduction in vegetation can occur without visible injury at about 0.25 ppm NO_2 although many species appear to be resistant at this level. A complicating factors is that in nitrogen deficient soils, NO_2 can be benefically converted to the nutrient, NO_3^-.

Visible injury occurs as chlorosis and necrosis, although the latter is seldom observed at normal environmental concentrations of NO_2. Some species exhibit chlorosis at 3 ppm, and most do at 32 ppm. The duration of the exposure is an important parameter. Dose is not always a good predictor of injury, and foliar injury is not always a specific predictor of damage. Chlorosis and necrosis may result from a number of environmental stresses. In some cases, leaf and stem weight may increase at the expense of fruit production.

In the atmosphere, NO and NO_2 may be converted to NO_3^-, which becomes nitric acid upon dissolution in rain water. Nitric and sulfuric acid are the major components of acid rain. Atmospheric deposition of nitrate may account for up to 30 kg N/ha·yr under the most extreme conditions, which may be 8 to 25 percent of the annual plant uptake in a forested ecosystem. Perturbation of the ecosystem would seem unlikely, then, if the atmosphere is a major source of an important nutrient. Two conditions are necessary for this beneficial effect: the nitrogen must reach the soil without injury to foliar tissues; and the nitrogen, by its acidic form, must not alter the chemical environment of the soil. There is evidence that neither of these conditions prevail. NO and NO_2 can cause undetected and visible foliar injury, and acid rain can alter the chemistry of soil, as discussed later.

Mixtures of nitrogen dioxide and sulfur dioxide can have a greater-than-additive or synergistic effect on plants. Whereas 2 ppm NO_2 or 0.5 ppm SO_2 did not cause foliar injury to a variety of crops, a mixture of 0.1 ppm of each caused foliar injury to pinto beans, radishes, soybeans, tomatoes, oats, and tobacco, with some injury detected at half these amounts.

There are four gaseous sulfur oxides known to occur in the atmosphere, but only sulfur dioxide (SO_2) is of significance as a pollutant. In contrast to other substances, the technology for measuring and predicting the distribution and deposition of SO_2 is moderately advanced. Most models for other pollutants are based on analogies to SO_2.

Sulfur dioxide is emitted in gaseous form from coal-fired power plants, primarily, as well as from other stationary industrial sources. It may be oxidized to sulfate (SO_4) where it becomes sulfuric acid upon dissolution in water, or SO_2 may adsorb to the surfaces of airborne particles. It may also remain in gaseous form until removed from the atmosphere.

As a gas, SO_2 may enter the leaf through the stomata and dissolve on the film of moisture surrounding the mesophyll cells, in a manner similar to ozone and NO_2. Sulfur dioxide is not as strong an oxidant and would probably simply alter the pH at the membrane surface. There is some evidence that SO_2 can cause stomata to remain open longer than normal, resulting in excess water loss by the plant leaf. Other evidence contradicts this phenomenon, and it is likely that the stomatal response depends on the absolute effect the SO_2 has on the stomatal cell membrane under the specific conditions present at the time of exposure.

At low concentrations, plants may incorporate, detoxify and utilize SO_2 taken in through the stomata. Within substomatal cavities, SO_2 reacts quickly with intercellular water to form sulfite and bisulfite. These are slowly oxidized to the less toxic sulfate. If the capacity of plant tissues to convert sulfite and bisulfite to sulfate is not exceeded or sulfate isolation processes are not overwhelmed, visible expression of SO_2 injury will not occur. This is in contrast to NO_2, which must be fixed to NO_3^- in the soil. Consequently, SO_2 may have a nutritive effect directly through the leaf or indirectly through the soil. Concentrations which cause no apparent adverse effect are about 160 $\mu g/m^3$

(0.06 ppm), or higher in certain sulfur deficient soils. But visible foliar injury may occur at concentrations slightly higher than that which gives the maximum biomass.

The first evidence of acute foliar injury is not chlorosis but a dark green, water-soaked appearance, suggesting a physiological response other than an interruption of chlorophyll production. Chlorosis may occur with chronic foliar injury, and necrosis is common in advanced stages of acute and chronic foliar injury.

This ability of plants to incorporate SO_2 as a source of nutrient sulfur under certain conditions complicates the problem of determining a dose-response level. No studies have been conducted which measure growth reduction and foliar injury in the context of all potential variables that can affect plant response. Also, the fact that a response has been measured at the subcellular level does not necessarily mean that an effect will be measured at the cellular or higher level of plant organization.

Yield reduction has been observed in soybeans at 800 $\mu g/m^3$ (0.3 ppm) chronic exposure. Wheat, barley and alfalfa exhibited no yield effects up to 400 $\mu g/m^3$ (0.15 ppm). Hot, humid conditions apparently increase the sensitivity of plants to SO_2.

Sulfur dioxide that is not incorporated by vegetation may reach the soil surface by direct deposition or by leaching from foliar surfaces. In the soil, SO_2 is oxidized to SO_4^-, where it becomes bound by organic matter. A portion of this organo-sulfur is exported out of the ecosystem in stream water.

Chronic exposure to SO_2 can result in an alteration of the nutrient cycling balance within an ecosystem, which can subsequently cause a reduction in population interaction such as species diversity. When an excess of a substance, even a nutrient, occurs in an ecosystem, the number of populations that can cope with this excess is less than the maximum number that can be supported by the ecosystem. In a lodgepole-jack pine forest, high sulfur concentrations in the soil, caused by nearby sulfur emissions, were correlated with lower foliar concentrations of Mn, P, K, Fe, Mg, N and Zn, but higher concentrations of Ca and Al.

Shrubs, cryptogamic flora and decomposer organisms are also affected by SO_2, sometimes at concentrations lower than those affecting trees. Some lichens are especially sensitive to SO_2, even at 50 $\mu g/m^3$ (0.02 ppm), possibly because they receive all of their nutrients from the atmosphere and are not adapted to high concentrations of sulfur.

For most plants, SO_2 demonstrates a synergistic effect with NO_2 and, to a lesser extent, ozone. The concentrations at which SO_2 and NO_2 are synergistic ($\sim$ 0.05 ppm each gas) are typically found in the ambient atmosphere of some parts of the United States.

Solid or liquid particles of matter originating from natural or anthropogenic sources affect terrestrial ecosystems primarily by adsorbing gaseous pollutants and transfering them to vegetation surfaces or to the forest floor. Small particles may also carry heavy metals to these surfaces.

Particles are transferred from the atmosphere to the earth by wet and dry deposition. The rate of dry deposition is a function of particle size, air concentration, windspeed, and surface roughness. Plant leaves are ideal depositional surfaces with their increased surface area and typical parallel orientation with the wind.

Although particles are typically emitted with a bimodal size distribution, the larger particles are removed from the atmosphere by gravitational sedimentation and the smaller particles agglomerate to an intermediate mode. Since the efficiency of agglomeration decreases with particle size, there is a maximum mean size for the intermediate or accumulation mode. It is with this distribution (0.1 to 0.5 μm in diameter) that particles are transported great distances.

The physical effect of particles on leaf surfaces could be to block stomata or to shade out sunlight. There is no evidence that either has a serious effect on the plant. Most plants leaves have stomata on the under surface of the leaf, and those on the upper surface represent less than 2% of the leaf surface area. The probability of a particle of exactly the right size lodging in a stoma is small.

If the particles or some of their chemical constituents are water soluble, it is possible that some of the pollutants will be dissolved and taken up through the stomata. It is more likely, however, that they will be leached from the leaf surface, passing to the base of the leaf or to the forest floor.

Metals deposited on leaf surfaces, if not absorbed across the cuticle layer or taken up through the stomata, eventually are transferred to the forest floor, where they are usually sequestered by soil organic matter. Entry into the plant is through the roots as these roots take up dissolved nutrients in soil moisture. Uptake by roots accounts for only a small fraction of the metal input to soils. Most metals are accumulated by soil in the organic layer.

Leaves are the first receptors of acid deposition in a terrestrial ecosystem. Particles bearing NO_x and SO_x are deposited on leaf surfaces, then converted to nitric or sulfuric acid in the presence of moisture. Leaves also intercept acid rain directly. The waxy cuticle layer on the leaf surface appears to be an effective barrier to acid rain, but if the acid solution penetrates the stomata or if the acid becomes concentrated on the leaf surface destroying the cuticle barrier, the leaf can be damaged.

Acid deposition not retained by the canopy is transferred directly to the soil surface. Many soils are naturally acid and most have a wide range of buffering capacity. The effect of acid deposition on soils is to shift the chemical equilibrium between the solid and liquid soil phase toward soil moisture. In other words, although the excess hydrogen ions of acid deposition may be readily incorporated into the solid phase of soil (organic particles and inorganic minerals), this is done at the expense of releasing nutrient and non-nutrient cations to the aqueous soil phase. This mobilization of the nutrient cations may deplete the soil as the water and nutrients percolate through the soil profile or pass out in the ground water.

A second effect of this shifting equilibrium is that concentrations of some elements in soil moisture may rise to toxic levels. These would be metals, such as Al^{+3}, weakly bound to the organic complexes of soil. At pH 4.4, Ca^{++}, Mg^{++} and Al^{+3} are freely released to soil moisture. In some cases, Al^{+3} may rise to toxic levels.

A third effect of acid in soil might be to restrict the growth of new roots. The root hair is the link between the nutrient soil moisture solution and the living tissue of the plant. It is a single-celled structure with no mechanisms to protect it from an adverse chemical environment. When a root hair successfully absorbs nutrients, the root elongates in that region and produces more root hairs. When a root hair dies, the root grows in a different direction, or stops growing altogether. Soils that are more acidic than normal present an adverse chemical environment to growing roots which limits the ability of plants to take up nutrients.

Soil acidity also affects decomposer and nitrogen-fixing microorganisms. Since nitrogen is often a limiting nutrient in soils, the loss of nitrogen-fixing organisms can seriously reduce the productivity of a terrestrial ecosystem. Low pH undoubtedly destroys some populations of decomposer microorganisms, but the ability of the soil to recover by the increased productivity of acid resistant decomposers is an important consideration. Often several decomposer populations perform the same role. The loss of one population does not seriously unbalance the decomposition process unless the affected population is a critical link to another portion of the decomposer food chains.

Acid deposition to agroecosystems, other than possible effects on leaf tissues discussed earlier, does not appear to be a problem. Nutrient mobility in these managed ecosystems is already so high that nutrients must be replenished artificially on an annual basis. Decomposers do not play a major role in cultivated soils and the possible toxicity of metals under acid conditions has not yet been experienced. The effects of acid deposition can probably be overcome with a small increase in the application of lime to the cultivated soil.

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